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**United States Patent**  
**Inoue , et al.**

**4,836,914**  
**June 6, 1989**

Method for removing iron content in petroleum series mineral oil therefrom

### Abstract

The present invention provides a method for removing an iron content in a petroleum series mineral oil therefrom which comprises treating a petroleum series mineral oil fraction containing 5 ppm or more of the iron content by the use of a high gradient magnetic separator under conditions of the strength of a magnetic field being from 500 to 25,000 gauss, a temperature being from room temperature to 400.degree. C., and a linear velocity being 0.1 to 50 cm/second.

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**Assignee:** Nippon Oil Co., Ltd. (JP)

**Appl. No.:** 240429

**Filed:** September 1, 1988

### Foreign Application Priority Data

May 08, 1985[JP]	60-97367
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<b>Current U.S. Class:</b>	208/251H; 208/177; 208/251R; 423/140
<b>Intern'l Class:</b>	C10G 045/04
<b>Field of Search:</b>	208/251 R,177,251H 423/140,151

### References Cited [Referenced By]

U.S. Patent Documents			
<u>2607492</u>	Aug., 1952	Anders	208/251.
<u>3696032</u>	Oct., 1972	Haensel	210/695.
<u>3767571</u>	Oct., 1973	Lorenc et al.	210/695.
<u>3923643</u>	Dec., 1975	Lewis et al.	208/251.

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**United States Patent****5,358,119****Stahl , et al.****October 25, 1994**

Method of separating a mixture of plastics comprising at least three components using electrostatic techniques

### Abstract

Plastic mixtures are split up into the individual components by a process combining density separation with electrostatic separation, and includes a special surface treatment which takes place prior to the electrostatic separation.

**Inventors:** **Stahl; Ingo** (Vellmar, DE); **Hollstein; Axel** (Kassel, DE); **Kleine-Kleffmann; Ulrich** (Bad Hersfeld, DE); **Geisler; Iring** (Bad Hersfeld, DE); **Neitzel; Ulrich** (Kassel, DE)  
**Assignee:** **Kali und Salz Aktiengesellschaft** (Kassel, DE)  
**Appl. No.:** **039273**  
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**PCT NO:** **PCT/EP92/01613**  
**371 Date:** **April 9, 1993**  
**102(e) Date:** **April 9, 1993**  
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**PCT PUB. Date:** **March 4, 1993**

### Foreign Application Priority Data

Aug 21, 1991[DE]

4127572

**Current U.S. Class:****209/3.1; 209/11; 209/127.4; 209/173****Intern'l Class:****B07C 005/02****Field of Search:****209/3,173,10,11,17,127.4,3.1**

### References Cited [Referenced By]

#### U.S. Patent Documents

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( 1 of 1 )

**United States Patent**  
**Reiniger**

**4,440,635**  
**April 3, 1984**

**Process and apparatus for the recovery of cellulose fibers from paper-plastic mixtures**

### Abstract

A process, and apparatus for recovering cellulose fibers from contaminated paper-plastic mixtures by exposing the mix to controlled wetting to increase the weight of paper cellulose components relative to the weight of the plastic components; subjecting the wetted mixture to abrasive forces to fiberize the paper component and then separating the fiberized paper cellulose product from the plastics and other contaminants, to yield several classified products showing distinctly improved quality.

**Inventors:** Reiniger; Haigh M. (320 Standish St., South Duxbury, MA 06901)

**Assignee:** Reiniger; Haigh M. (Old Lyme, CT); Moller; Toste W. (Rowayton, CT)

**Appl. No.:** 231263

**Filed:** February 3, 1981

**Current U.S. Class:** 241/19; 209/4; 209/32; 209/306; 209/930; 241/20; 241/21;  
241/79.1; 241/86.1; 241/DIG38

**Intern'l Class:** B02C 023/14

**Field of Search:** 209/3,4,12,32,33,245,273,306 241/19-  
21,24,28,74,79,79.1,86.1,188 R,154,DIG. 38

### References Cited [Referenced By]

#### U.S. Patent Documents

<u>3856217</u>	Dec., 1974	Brewer	241/79.
<u>4072273</u>	Feb., 1978	Reiniger	241/24.
<u>4160722</u>	Jul., 1979	Marsh	241/20.

#### Foreign Patent Documents

2547008	May., 1976	DE	241/188.
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*Primary Examiner:* Hill; Ralph J.

*Attorney, Agent or Firm:* Bryan; Roland T.

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steps, whereby in a first step, the plastic particles having a different density range are separated from each other, and whereby in a second step, the plastic particles with the same density range are separated. In this connection, the plastic particles are advantageously separated in the first step according to the principle of density separation, whereby the density of the separation liquid is selected in such a way that it falls in the field of the greatest density difference between the individual plastic types of the plastic mixture; advantageously, the density of the separation liquid is adjusted in this connection between 1.0 and 1.3 g/cm<sup>3</sup>. The density separation can take place in this connection by means of a hydrocyclone as well. If necessary, the separation according to the density takes place not only in one step but in several ones if several types of plastic with a different density are to be separated.

Furthermore, it has been found that it is possible to achieve through a surface treatment of the plastic particles of the plastic mixture an improved triboelectric charging in the sense of a higher charge density.

According to an advantageous feature of the invention, the chemical treatment of the surface of the plastic particles of the plastic mixture takes place in that the separation liquid is selected in such a way that it is in the basic range (pH about 10 to 12) or in the acid range (pH of 2 to 4). Particularly advantageous results are obtained if the separation liquid is a salt solution of which NaCl is the main component. In addition to the NaCl in the salt solution, K-, Mg- and SO<sub>4</sub>-ions may be present in the salt solution as well, i.e., because of the desired composition of the salt solution it is possible to use a salt solution as formed as a waste product in the production of potash in potash mining. An enhanced triboelectric charging is particularly achieved also if, after the density separation, the separation liquid is washed out of the plastic mixture by water. In the course of density separation or of the subsequent cleaning of the plastic mixture with water, the plastic particles having a size of under 10 and preferably about under 6 mm can be cleaned from paper residues or beverage residues. However, such cleaning is possible also in a washing process carried out prior to the density separation, for example in a washing mill or in a turbo-washer. After the washing, a drying of the plastic mixture takes place, whereby prior to the actual drying, the water content of the plastic mixture is reduced by a dehydration aggregate, e.g. a centrifuge, to a residual water proportion of under 2%.

In the following, the plastic mixture is subjected to a thermal treatment at 30.degree. to 100.degree. C. over a time period of at least 5 minutes; this measure, too, serves for achieving a higher charge density of the individual plastic particles. This is seemingly explainable in that due to the thermal treatment in the aforementioned temperature range, a change occurs in the surface of the plastic particles. The surface treatment can be achieved both chemically and through heat, or through both types of treatment.

According to another advantageous feature of the invention, an organic substance, in particular fatty acid is added to the plastic mixture in an amount of about 10 to 50 mg/kg plastic mixture. The addition of fatty acid serves for the conditioning of the plastic particles, also with the objective of obtaining in the subsequent triboelectric charging a higher charge density of the individual particles. This treatment, too, can take place alone or in combination with the chemical or thermal treatment of the plastic particles.

It has been found that with plastic particles pretreated in said way, only field intensities of 2 to 3 KV/cm have to be maintained in the free-fall separator itself.

As opposed to the above, the free-fall separator operates in connection with the known process with a field intensity of 3 to 4 KV/cm, which posed the danger of spray discharges. Spray discharges may cause an ignition of the plastic mixture in the free-fall separator.

The triboelectric charging itself takes place, for example in a fluidized-bed dryer, or in a spiral worm of adequate length, or also by pneumatically conveying the plastic mixture over a certain distance. As



## BACKGROUND OF THE INVENTION

### 1. Field of the Invention

The invention relates to a process for the separation of plastic particles of a plastic mixture of plastics of a chemically different type which partly have an overlapping and partly a different density range, e.g. polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC).

### 2. The Prior Art

Such different types of plastic occur as waste, for example when different one-way bottles are mixed. For example, still waters are predominantly filled in 1.5-liter PVC-bottles, whereas other beverages are sold in so-called PET-bottles. In Western Europe alone, 1.4 billion PET-bottles are manufactured annually. The bottles have, as a rule, a polyethylene screw cap, whereby the PET-bottles may have a bottom part made of polyethylene as well. Direct recycling of the mixed bottle plastics is not possible because PET melts only at 260.degree. C., whereas PVC decomposes with separation of HCl already above the softening temperature of 160.degree. C. There are, therefore, no appreciable recycling possibilities, so that the waste plastics have not been collected heretofore but eliminated via the household refuse, i.e., they are finally incinerated or deposited.

Furthermore, it is not possible, as a rule, to achieve any profits for mixed PVC-containing plastics. The fact is rather that the reuser frequently demands a credit that is oriented on the dumping costs saved.

As opposed to the above, there is a market for purely sorted recycling plastics since long, whereby the prices are oriented on the prices for new material. Up to 60% of the new material is achieved for recycling material depending on the quality. Thus there is much interest in processes for the separation of mixed plastics.

The processes known from the state of the art for the separation of plastic particles of plastics of a chemically different type operate with plants separating according to the density, for example hydrocyclones. Said process, however, fails in connection with plastics that are in the same density range such as, for example, PET (density about 1.37 to 1.38 g/cm.<sup>sup.3</sup>) and PVC (density about 1.38 g/cm.<sup>sup.3</sup>). However, the separation of polyethylene (PE) from the other two plastic types PET and PVC is possible because of the different density of 0.95 g/cm.<sup>sup.3</sup>. The separation of plastics that are in the same density range can be carried out, for example electrostatically.

It is known from DE-PS 30 35 649 to separate plastics electrostatically in a free-fall separator.

However, it has been found that in the separation of a plastic mixture with three or four different types of plastics, thus for example PE, PET, PS and PVC with one of said processes, a large quantity of medium material is collected, or that the deposits on the respective electrode have only an insufficient degree of purity. Furthermore, the medium material has a high component of at least one of the plastics used.

## SUMMARY OF THE INVENTION

The invention, therefore, has the object of creating a process of the type specified at the beginning in which several components of a plastic mixture even of similar or the same densities can be safely separated from one another. This object is achieved in that the separation takes place in at least two

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J1017 U.S. PTO  
10/092281  
03/06/02

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**United States Patent**  
**Kreisler**

**6,270,679**  
**August 7, 2001**

**Method for recovering and separating metals from waste streams**

### Abstract

A method is disclosed for recovering and separating precious and non-precious metals from waste streams, which removes, separates, and recovers such metals in a cost effective manner with more than 95% removal from waste streams and with minimal amounts of unprocessed solids and sludge remaining in the environment. Metals such as chromium, manganese, cobalt, nickel, copper, zinc, silver, gold, platinum, vanadium, sodium, potassium, beryllium, magnesium, calcium, barium, lead, aluminum, tin; and the like are removed and recovered from the waste streams with at least 95% removal and other metals and compounds, such as antimony, sulfur, and selenium are removed and recovered from waste streams with at least 50% removal. The method employs a unique complexing agent comprising a carbamate compound and an alkali metal hydroxide which facilitates the formation of the metals into ionic metal particles enabling them to be readily separated, removed and recovered. The method disclosed is also applicable to recover metals and other compounds originating from different waste sources such as existing and abandoned mines, contaminated ground water, standing contaminated water, and waste streams having a high solids content as well as treating water intended for potable use, recovering metals and other compounds from polluted or contaminated air, and the like. In addition, the disclosed method can be used to separate and recover precious and non-precious metals present in waste waters resulting from steel manufacturing, battery and chemical manufacturing, printed circuit board waste, titanium pickle operations, nickel and chrome plating operations, electroless nickel operations, X-ray and photographic waste, aluminum anodizing operations, construction and demolition landfill leaches, and the like. The method of the invention can also be used to recover metals from highly acidic waste streams or other process liquids without adjusting the pH of said streams or liquids and to separate and recover metals from otherwise unusable hazardous materials. Further, the method of the invention can be utilized in a multi-stage recovery system to selectively separate and recover targeted metals at even higher efficiencies.

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**Appl. No.:** **229318**

**Filed:** **January 13, 1999**

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423/101

**Intern'l Class:** G02F 001/62

**Field of Search:** 75/416,417 204/DIG. 13  
210/709,710,719,720,721,723,724,725,726,727,728,743,912,913,914  
423/92,104,101

### References Cited [Referenced By]

#### U.S. Patent Documents

<u>3899322</u>	Aug., 1975	Yosim et al.	75/65.
<u>3966601</u>	Jun., 1976	Stevenson et al.	210/53.
<u>4135923</u>	Jan., 1979	Day	75/153.
<u>4260493</u>	Apr., 1981	Krefas et al.	210/714.
<u>4364773</u>	Dec., 1982	Veronneau et al.	423/34.
<u>4387034</u>	Jun., 1983	Unger et al.	252/61.
<u>4406696</u>	Sep., 1983	Hans et al.	75/72.
<u>4465593</u>	Aug., 1984	Wemhoff	210/96.
<u>4561887</u>	Dec., 1985	Domic et al.	75/72.
<u>4578195</u>	Mar., 1986	Moore et al.	210/679.
<u>4612125</u>	Sep., 1986	Elfline	210/724.
<u>4678584</u>	Jul., 1987	Elfline	210/719.
<u>4724084</u>	Feb., 1988	Pahmeier et al.	210/709.
<u>4943377</u>	Jul., 1990	Legare, III	210/709.
<u>4957634</u>	Sep., 1990	Bowers, Jr.	210/711.
<u>5000858</u>	Mar., 1991	Manning et al.	210/709.
<u>5008017</u>	Apr., 1991	Kiehl et al.	210/710.
<u>5039428</u>	Aug., 1991	Wentzler et al.	210/711.
<u>5045213</u>	Sep., 1991	Bowers	210/709.
<u>5128047</u>	Jul., 1992	Stewart et al.	210/724.
<u>5177304</u>	Jan., 1993	Nagel	588/201.
<u>5178772</u>	Jan., 1993	Daley et al.	210/721.
<u>5191154</u>	Mar., 1993	Nagel	588/201.
<u>5202100</u>	Apr., 1993	Nagel et al.	423/5.
<u>5205939</u>	Apr., 1993	Syrinek	210/727.
<u>5264135</u>	Nov., 1993	Mohn	210/710.
<u>5298168</u>	Mar., 1994	Guess	210/713.
<u>5298233</u>	Mar., 1994	Nagel	422/129.
<u>5301620</u>	Apr., 1994	Nagel et al.	100/346.
<u>5322547</u>	Jun., 1994	Nagel et al.	75/414.
<u>5324341</u>	Jun., 1994	Nagel et al.	75/503.
<u>5354940</u>	Oct., 1994	Nagel	588/201.
<u>5358549</u>	Oct., 1994	Nagel et al.	75/414.

<u>5358697</u>	Oct., 1994	Nagel	422/184.
<u>5364441</u>	Nov., 1994	Worner	75/10.
<u>5372726</u>	Dec., 1994	Straten	210/728.
<u>5395405</u>	Mar., 1995	Nagel et al.	48/92.
<u>5401420</u>	Mar., 1995	Siefert et al.	210/709.
<u>5435982</u>	Jul., 1995	Wilkinson	588/201.
<u>5436210</u>	Jul., 1995	Wilkinson et al.	588/201.
<u>5443572</u>	Aug., 1995	Wilkinson et al.	266/46.
<u>5505857</u>	Apr., 1996	Mirsa et al.	210/709.
<u>5510040</u>	Apr., 1996	Miller et al.	210/721.
<u>5545331</u>	Aug., 1996	Guess	210/713.
<u>5753125</u>	May., 1998	Kriesler	210/710.
<u>5908559</u>	Jun., 1999	Kriesler	210/710.

#### Foreign Patent Documents

WO 91/08023	Jun., 1991	WO.
WO 93/02750	Feb., 1993	WO.
WO 93/25277	Dec., 1993	WO.
WO 93/25278	Dec., 1993	WO.
WO 95/17359	Jun., 1995	WO.
WO 95/17360	Jun., 1995	WO.
WO 95/17362	Jun., 1995	WO.

*Primary Examiner:* Hruskoci; Peter A.  
*Attorney, Agent or Firm:* Feldman; Stephen E.

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#### Parent Case Text

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#### FIELD OF THE INVENTION

This application is a continuation-in-part of co-pending application Ser. No. 09/122,665 filed Jul. 27, 1998 which, in turn, is a continuation-in-part of application Ser. No. 09/080,556 filed May 18, 1998 which, in turn, is a continuation-in-part of application Ser. No. 09/003,417 filed Jan. 6, 1998 now U.S. Pat. No. 5,908,559 which, in turn, is a continuation-in-part of application Ser. No. 08/696,321 filed Aug. 13, 1996, now U.S. Pat. No. 5,753,125, which, in turn, is a continuation-in-part of application Ser. No. 08/445,353 filed May 19, 1995 now abandoned.

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#### Claims

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What is claimed is:

1. A process for separating and recovering metals from acidic waste streams and acidic process liquids comprising:

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- (a) feeding an acidic waste stream or acidic process liquid into a chamber, said acidic waste stream or acidic process liquid containing metals including cadmium and lead and having a pH of from about 0.0 to about 4.0;
- (b) adding a complexing agent to said acidic waste stream or acidic process liquid to form metal ion complexes in said waste stream or process liquid to cause said metals to precipitate in the form of a sludge, said complexing agent being a mixture of water, an inorganic base selected from the group consisting of sodium hydroxide, calcium hydroxide and potassium hydroxide and a thiocarbamate or dithiocarbamate selected from the group consisting of sodium dimethyldithiocarbamate, zinc dimethyldithiocarbamate, and mixtures thereof;
- (c) dewatering and drying said sludge to a substantially anhydrous state; and,
- (d) melting said dewatered and dried sludge to recover said metals therefrom.

2. The process of claim 1 wherein the metals recovered are members selected from the group consisting of aluminum, arsenic, cadmium, chromium, lead, iron, nickel and zinc.

3. The process of claim 2 wherein said cadmium and said lead are recovered at efficiencies of greater than about 95% and the remainder of said metals are recovered at efficiencies of from about 18% to about 58%.

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### *Description*

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The present invention relates generally to a method for removing precious and non-precious metals from hazardous and non-hazardous waste streams, and more particularly to a method for recovering and separating such metals from different types of waste streams.

## BACKGROUND OF THE INVENTION

Treatment and reduction of concentrations of metals in metal bearing industrial waste streams to environmentally acceptable levels has been a long term problem. It is important to be able to treat such wastes and remove metals, hazardous materials, and toxic substances, with minimal amounts of solid wastes remaining in a cost effective manner. The ultimate solution to such environmental problems, recovery, recycling, and reuse of metals contained within waste streams has been inadequately addressed.

In those instances where metals, compounds, and hazardous materials are not separated from waste streams, but are transported to special waste disposal facilities for treatment or storage, the metals are not recovered, leaving them to be disposed of with other unprocessed or partially processed wastes. As a result, not only is there no recycling with the attendant potential for economic profit or cost reduction, but waste disposal and waste storage problems are created as well. Such waste disposal and waste storage problems are associated with high cost and long waste storage time periods. Often, the wastes generated are considered to be hazardous. Under many environmental statutes, hazardous, toxic, and/or dangerous wastes remain the liability of the waste generator, as long as these wastes exist in the environment. Such long term liability remains with the generator, even though the wastes may have been treated and placed in a secure landfill for disposal.

Processes for removing metals from waste streams including ion exchange and electrolysis have heretofore been known, but these processes are limited. Ion exchange is costly, slow, and cumbersome to use, and in order to be effective, the waste water being treated must be passed through a significant amount of ion-exchange resin, usually in the form of a filter bed, making it effective, in most cases, for only treating small volumes of waste water. The complex fabrication process and sophisticated synthetic chemistry required by ion exchange metal recovery technology significantly contributes to the expense of its use to purify liquid waste streams. The cost and complexity of ion exchange also limits the variety of resins available.

Although ion exchange resin beds may be regenerated, the waste waters from regeneration must often be retreated to remove bulk contaminants and then usually passed through the ion exchange resin again to eliminate hazardous materials. Thus, ion exchange is a cumbersome process, and therefore impractical, especially for large volumes of waste water in a continuous-treatment process, as compared to using ion-exchange in a batch-treatment process.

Electrolysis is also expensive, requires significant maintenance, employs other resources, may create its own waste disposal problems and is energy intensive. Electrolytic recovery is, at best, 70%-80% efficient. Besides, the electrolyte systems available today are very sensitive to the presence of contaminants.

Use of either ion exchange or electrolytic recovery of metals from waste streams requires separation of streams for processing, thereby ultimately creating multiple waste streams. This multiplicity of streams results in a costly waste removal process for the waste stream generator.

In contrast to the ion exchange and electrolytic metal recovery processes, one of the more acceptable technologies for treating waste water is based on a settling process, using fixating agents such as hydroxides and sulfates. The fixating chemicals are added to water in a settling tank to absorb or otherwise transform the contaminants into materials which settle to the bottom of the tank. This technology uses comparatively simple equipment and permits the processing of large volumes of waste waters, without adding materials which would result in an environmentally undesirable effluent stream. However, in many cases, use of ordinary settling processes fails to reduce contaminant concentrations to levels low enough to meet the statutory requirements, without using excessive amounts of materials, over a protracted processing time. Current settling processes often produce undesirably large quantities of solid hazardous or toxic wastes in the form of sludge. The sludge cannot, for the most part, be effectively regenerated. Thus, using current settling techniques for waste water treatment, the resulting sludge product is yet another waste material that must be disposed of in a secure landfill without benefit of recycling. In turn, this process results ultimately in the necessity to clean the environment in the long term future.

As a result of problems associated with the above noted technologies, waste water generators have been forced to consider alternative methods which employ the addition of metal complexing agents to waste water streams and sludge of various industrial processes.

For example, U.S. Pat. No. 3,966,601 (Stevenson, et al.) discloses a purification process comprised of mixing a soluble heavy metal salt and a heavy metal dithiocarbamate. U.S. Pat. No. 4,387,034 (Unger, et al.) discloses a collector for use in concentrating metal values in ores by flotation, the collector being comprised of a mixture of O-isopropyl N-ethylthionocarbamate and o-isobutyl N-methylthionocarbamate.

U.S. Pat. No. 4,578,195 (Moore, et al.) discloses a process for treating aqueous effluents to remove polluting metallic elements wherein the effluent is contacted with a poly(dithiocarbamate) chelating

agent. U.S. Pat. No. 4,612,125 (Elfline) discloses a method for removing heavy metals from waste water streams, comprising treating the waste water with sulfur-containing compounds, such as sodium tri-thiocarbamate.

U.S. Pat. No. 4,678,584 (Elfline) discloses a method for treating a liquid containing a heavy metal comprising contacting the liquid with a mixture of sodium diethyldithiocarbamate and sodium tri-thiocarbamate. U.S. Pat. No. 4,943,377 (Legare) discloses a method for removing heavy metals from waste effluents comprising mixing the effluents with a solution of a sulfur compound such as sodium polythiocarbamate. U.S. Pat. No. 5,372,726 (Straten) discloses a method for treating water polluted by metal ions comprising the steps of adding thiocarbamide, potassium or sodium hydroxide, and potassium or sodium hyposulfite.

U.S. Pat. No. 5,264,135 (Mohn) discloses a method for treating sludge from industrial waste water streams comprising the steps of adding a metal complexing agent to the sludge such as dimethyl-dithiocarbamate or a salt thereof. The metal complexing agent is added to a sludge thickening tank prior to de-watering in a filter press to form a sludge that contains 60% to 85% moisture by weight. Mohn does not disclose use source separation of the effluent throughout the process and does not disclose adjusting the pH of the waste solution to the optimal point of insolubility for the various metals involved. Mohn characterizes the sludge as being fixated, thereby allowing disposal in landfills.

In addition, a number of metallurgical processes for recovering metal have also been disclosed. For example, U.S. Pat. No. 3,899,322 (Yosim et al.) discloses a process for recovery of noble metals from scrap comprising melting the scrap at a temperature between 800.degree. F. and 1,800.degree. F. U.S. Pat. No. 4,135,923 (Day) discloses a process for the extraction of metals from metallic materials comprising heating a lead-free mixture of metals and separating the metals in a molten state.

U.S. Pat. No. 5,008,017 (Kiehl, et al.) discloses a process for recovering metals from waste liquids, including a step for obtaining pure metal. A dewatered sludge is heated for a period from about thirty minutes to about one hour at 900.degree. F., to recover substantially pure silver. However, this metallurgical process for recovering metals from a metallic sludge is very complicated, and requires a metal complexing agent be applied to the metallic sludge of waste streams.

None of the known prior art technologies separate and also recover a variety of metals from one or more waste streams in order to use the metals as valuable commercial products, nor do they disclose the recovery, recycling, and reuse of the recovered metals. In those prior art processes using reagents to cause fixation of metals and to produce a fixated hydroxide sludge byproduct, the resulting byproducts must be sent to and disposed of in a secure landfill or alternative receiving site.

For the foregoing reasons, there is a need for a method for removing, separating, and recovering metals and groups of metals, such as transition metals, alkali metals, and alkaline earth metals. An efficient method for removing, separating, and recovering such metals in a cost effective manner with a high degree of recovery from waste streams and with minimal amounts of unprocessed solids and sludge remaining in the environment is needed.

Illustrative, but not limitative, of the precious and non-precious metals and other compounds that such a method can be capable of separating, removing and recovering are aluminum, antimony, arsenic, barium, beryllium, calcium, chromium, cobalt, copper, gold, iron, lead, magnesium, manganese, mercury, nickel, platinum, potassium, silver, sulfates, tin, vanadium, zinc, and the like. Such a process should also be capable of removing such metals and compounds from waste streams with at least 50% removal.

## SUMMARY OF THE INVENTION

The present invention is directed to a method for recovering and separating precious and non-precious metals from hazardous and non-hazardous industrial waste streams. The method of the present invention removes, separates, and recovers such metals in a cost effective manner with more than 95% removal from waste streams and with minimal amounts of unprocessed solids and sludge remaining in the environment.

The method of the present invention for separating and recovering precious and non-precious metals and other compounds from industrial waste stream generally comprises: adjusting the pH of an industrial waste stream containing the precious and non-precious metals and other compounds to be recovered; adding a metal complexing agent to said waste stream to form metal ions of the metals to be recovered; adding a particle growth enhancer to promote the aggregation of said metal ions; adding a flocculating agent to increase the particle size of said metal ions and form a solution thereof; dewatering said solution to form a sludge and a supernatant; dewatering and drying said sludge to form a metal concentrate; and, melting said concentrate to selectively remove and recover a desired metal therefrom.

It has also been found that the method of the present is applicable to the recovery of desired metals and other compounds generated from different waste sources. For example, the method of the present invention has been found to be useful in treating waste streams originating from existing and abandoned mines, operating and active mines and other ore extraction processes, contaminated ground water, standing contaminated water such as is found in ponds, lagoons, pits, and the like, waste streams containing low level radioactive metals, and waste streams having a high degree of solids in solution as well as treating water intended for potable use and separating and recovering metals and other compounds from polluted or contaminated air.

In one embodiment, the method of the invention is applicable to the separation and recovery of metals, non-metallic elements and other compounds from various types of wastewater. For the purposes of this embodiment, wastewater is defined as any aqueous solution containing inorganic and organic contaminants and other compounds in amounts sufficient to render the solution unfit for introduction into the environment and/or consumption by or exposure to plant, animal or human life. In general, these waste waters can be treated as follows:

### A. Preparatory Treatment

1. Remove insoluble organic material and/or
2. Subject the wastewater to oxidation/reduction agents and/or
3. Adjust the pH of the solution and/or
4. Add an aggregating agent and/or
5. Add an ion exchange promoter

### B. Separation

1. Add a carbamate complexing agent to the solution and/or
2. If required, add a non-carbamate complexing agent such as sodium sulfide or a polythiocarbonate to the solution and/or



3. Add an aggregating agent and/or
4. Add a polymeric flocculent
5. Discharge or recover the clean effluent for reuse

#### C. Recovery and Reclamation

1. Draw off the separated material and dewater to reduce moisture content and obtain a dense ore quality solid and/or
2. Dry the dense ore quality rich solid to further reduce moisture content and/or
3. Route the dense ore quality rich solid to a consumer or end user and/or
4. Produce a metal rich ingot from the dense ore quality rich solid

In the general treatment described above, the various steps have been set forth as being additive or alternative since specific treatment steps will be dependent upon the nature of the wastewater being treated. For example, depending upon the source of the waste water to be treated, all of the preparatory treatment steps can be by-passed and the wastewater can be subjected directly to the separation steps.

In another embodiment, the method of the invention is used to selectively recover cadmium and lead from highly acidic waste streams or other process liquids having a high acidic content; i.e., a pH of from about 0.0 to about 4.0, without adjusting the pH of the waste streams or process liquids. This method can be readily used in such applications as the manufacture and production of fertilizers, lead-acid batteries, polishing of micro-nutrients, and the like.

In a further embodiment, the method of the invention is used to recover and reclaim metals and other compounds from otherwise unusable hazardous materials such as hazardous sludge, dredge materials, incinerator ash, and the like.

In still another embodiment of the invention, the method of the invention is used to selectively remove and recover greater than 95% of targeted metals and thereby enhance the quality and salability of the recovered metals. In this embodiment, a metallic complexing agent of the invention is employed to selectively separate and remove the targeted metals in pre-determined quantities at different stages.

#### DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, a method for recovering and separating metals from waste streams, comprises the following steps:

pH of a waste stream is adjusted;

a metal complexing agent is added;

an aggregating agent is added;

a flocculating agent is added resulting in a solution;

the solution effluent is then dewatered, preferably using a plate and frame press, resulting in a sludge and a supernatant; and

metals are recovered from the sludge upon melting, drying and dewatering a filter cake with melting enhancers so as to permit selective removal of a fused metal-bearing concentrate for casting into ingots to be sold to primary smelters.

A suitable base such as sodium hydroxide (NaOH) or calcium hydroxide (Ca(OH)<sub>2</sub>) or a suitable acid such as hydrochloric acid (HCl) can be used to alter the solubility of the metal or compound to be recovered by altering the pH of the waste stream from about 5 to about 13, preferably from about 7 to about 12, depending upon the initial pH of the Waste stream to be treated and the metal(s) or compound(s) desired to be recovered.

The metal complexing agent that can be used comprises a mixture of a carbamate compound, an inorganic base, and water. The carbamate that can be employed are those selected from the group consisting of thiocarbamates, dithiocarbamates, alkylthiocarbamates such as dimethyldithiocarbamate and diethyldithiocarbamate, and salts thereof. The inorganic bases that can be used are those selected from the group consisting of sodium hydroxide, calcium hydroxide, potassium hydroxide, and the like. A preferred complexing agent comprises a mixture consisting of about 40% by weight sodium dimethyldithiocarbamate; about 10% by weight sodium hydroxide; and, about 50% by weight water.

The aggregating agent is employed to promote an ionic exchange with the metals in solution and to provide a foundation upon which the ionic metal particles can grow. The preferred particle growth enhancer used is an aqueous solution of calcium chloride comprising about fifty pounds (50 lbs.) calcium chloride dissolved in about 100 gallons (gals.) of water in combination with an ionic exchange promoter. The ionic exchange promoter employed is ferric chloride (FeCl<sub>3</sub>) which is commercially obtained as a 38% liquid solution. The amount of ionic exchange promoter used can range from about 0.03% to about 0.4% by volume.

The flocculating agents employed in the method of the present invention are commercially obtained material typically available as solid, granular ionic polymers having a medium anionic charge. These flocculating agents, together with the particle growth enhancer and the ionic exchange promoter, cause the ionic metals in solution to increase in size and weight, precipitate, and settle. Illustrative flocculating agents that can be used include Clarifloc A-3020 available from Poly Pure, Inc., Parsippany, N.J.; Flocculite 402 available from Dubois, Cincinnati, Ohio, and J. Flock 711 available from Jamestown Chemical, Westhaven, Conn. The flocculating agent is prepared as a diluted aqueous solution consisting of one pound of the flocculating agent in 65 gallons of water and then further diluting this concentrate in 200 gallons of water. This dilute solution is then used in concentrations of from about 0.001% to about 0.01% by volume. The preferred flocculating agent employed is Clarifloc A-3020.

When the industrial waste stream to be treated contains organic compounds, they are initially degraded or destroyed by using a suitable oxidizing agent such as sodium hypochlorite, hydrogen peroxide at 35% to 50% concentration, ultra violet (UV) radiation or ozone (O<sub>3</sub>). When an oxidizing agent is used, the waste stream should be monitored to assure that an oxygen reduction potential (ORP) of about +350 mv is achieved and maintained for a period of about 15 minutes before treating the waste stream with the method of the invention.

Similarly, when the industrial waste stream to be treated is found to contain chelating agents (e.g., hexavalent chromium) these agents are initially degraded or destroyed by using a suitable reducing agent such as sodium metabisulfite, sodium sulfide, and the like. The waste stream should be monitored until the presence of the undesirable chelating agent can no longer be detected.

The method of the invention includes the following steps:

a. Waste streams to be treated are analyzed to determine the types of wastes and metals present, whether the waste streams contains precious metals or non-precious metals; volatile organic compounds (VOCs); solids above 5% by volume, chromium above an average of 15 parts per million (ppm); and cyanide.

All incoming wastes are classified by priority metal which in a given waste solution to be treated, is the metal found most prominently. The most prominent metal is analytically identified. For example, a waste solution containing 1000 ppm of copper and 200 ppm of cadmium has copper as the priority metal and cadmium as the secondary metal.

b. Incoming waste streams are separated according to the priority metal, identified by the analytical procedures for each respective waste stream. Waste solutions with common dominant metals are mixed together for processing. For example, a solution containing 1000 ppm or more of copper is mixed only with a waste solution containing a priority metal of copper, since to do otherwise would reduce the concentration of copper in the final metal recovery product. Recovery product is sold to primary smelters based on the level of the priority metal. As the priority metal is removed, the secondary metals are all concentrated and the process moves to the next level based on the new priority metal selected from the remaining waste solution. Thus, a continuing recycling process takes place removing each priority metal successively.

c. The pH of the waste streams is adjusted, as required, to increase insolubility of the priority metal with ionically bonded compounds and to precipitate ionic metal particles upon addition of a reagent. The optimum pH level will vary from 7 to 12 depending on the priority metal being addressed in the waste solution. For purposes of selective separation, the priority metal is the most prominent metal determined by analysis, i.e., the metal which the aforementioned analysis reveals to be present in the highest concentration.

d. The reagent, in the form of a metal complexing agent is added to chelate certain metals from ionically bonded compounds. These metals will ultimately be removed and recovered from the waste water. The metal complexing agent comprising a dithiocarbamate and preferably comprising about 40% sodium dimethyl dithiocarbamate, about 10% sodium hydroxide (NaOH) and about 50% water is used.

e. In the continuous treatment process described herein, 30 gallons of the aqueous calcium chloride particle growth enhancer solution is first added to a primary reaction tank containing 1,400 gallons of waste water as described herein below. When the contents of the tank are processed, CaCl.sub.2 is added to the flash mix tank continuously.

f. When the ferric chloride ionic exchange promoter is used, it is added to the primary reaction tank used during the continuous treatment process and is also added directly to the tank in the batch treatment process.

g. Sodium hydroxide (NaOH) or calcium hydroxide Ca(OH).sub.2 is added to the mix, the choice of which to use depends on the solution's sensitivity to pH change. A solution which is heavily buffered (resistant to pH of change) is first treated with Ca(OH).sub.2 and then fine-tuned with NaOH. On the other hand, a solution that has little or no buffering and is thus sensitive to pH change, will be adjusted with NaOH only. The hydroxide is added to adjust pH to the optimum level for the priority metals, as discussed more fully below;

h. As described above, flocculating agents are added to the mix, as described below, to cause the ionic

metallic precipitant to increase in size and weight and settle.

As the diluted working solution is used, proportional amounts of the flocculent concentrate and water are added to replenish the working tank as make-up flocculating agent.

The flocculent polymer solution is added to the continuous treatment process by injecting it into the flash mix tank on a continuous basis. The amount of flocculent polymer added is in proportion to the amount of dissolved and suspended solids in the waste being treated. The flocculant is preferably used in concentrations ranging from about 0.0001% to about 0.01%.

i. Oxidation and reduction are used, as required. Waste solutions containing both hexavalent chromium and cyanide ions, such as certain plating solutions, requires oxidation first and reduction second to ensure that metal separation is complete. Thus, there are cases requiring both oxidation and reduction.

In those cases where oxidation and/or reduction is required prior to processing the wastes, the wastes are first processed in a batch operation as described under "Batch Treatment" below.

j. Heavy particles settle, resulting in a sludge and the supernatant is clarified and discharged. The sludge is thickened and dewatered, and metals are recovered from the resulting thickened and dewatered sludge as described below.

k. The present invention recovers metals in the form of a dried powder. The metal-recovered dried powder may be either melted as specified and preferred in the present invention or, alternatively, the metal-recovery dried powder may be sold to the smelter, where the product is used as a feed stock in place of a virgin product in the smelting operation.

The final and preferred step in the metal recovery of the present invention occurs with the melting of the metal compounds. A flux, preferably a mixture of sodium tetra borate pentahydrate and soda ash, is added to facilitate this melting step. Sodium tetra borate decahydrate and sodium tetra borate anhydrous may be used in place of sodium tetra borate pentahydrate. The metal compounds are melted and then allowed to cool, resulting in solid recovered metal products.

The resulting metals are recovered and separated by primary metal and are sold to secondary and primary smelting operations. The present invention provides the raw material feed stock for the smelting recovery of the metals recovered as ionic compounds from waste streams. For example, a recovered product containing copper as the primary metal is sold to a primary copper smelter.

Waste streams containing large amounts of metals such as concentrations equal to or greater than 2000 ppm (0.02% dissolved solids) and specific solutions such as photographic wastes are treated in batch. In the batch treatment, all operations occur in the same treatment vessel, i.e., a volume of waste is placed in a tank, reagent is added, and the solution is allowed to settle, leaving the clean supernatant at the top and prepared and/or ready for discharge.

In comparison to batch treatment, continuous treatment is used for waste solutions and in those cases where the volume of the waste stream is in excess of 2000 gallons. In continuous treatment the waste solution is treated in different tanks, each tank being used generally for a different purpose. The wastes are moved from one tank to another allowing sufficient residence time for the solution to be processed in each tank and for the required chemical processes to take place. Solutions move at rates varying from about 5 gallons per minute [gpm] to about 5000 gpm depending on the level of dissolved solids being removed from the solution.

In continuous treatment, the wastes are moved from a primary treatment tank to a flash mix tank, to a flocculation tank, then to a gravity settler tank, then to a filtration system, and finally to discharge. The solids that settle in the gravity settler are continuously removed to a sludge settling tank prior to dewatering. Continuous treatment operation is used to move large volumes of waste containing low levels of dissolved contaminants rapidly through treatment.

Both the continuous treatment and batch treatment operations produce sludge. The amount of sludge produced is directly related to the amount of dissolved metal in the incoming waste. As an example, a solution containing one pound of dissolved salts will produce approximately one pound of sludge. Moreover, an input containing 60,000 mg/liter of copper and 0.15 mg/liter of lead would be typically left with 0.8 mg/liter copper and 0.02 mg/liter lead, which means that 59,999.02 mg/liter copper and 0.13 mg/liter lead could be recovered by the process of the present invention. In such case, the recovery rate for copper is 99.9987% and for lead 86.666%.

The method of the invention is based upon the ability of the carbamate compounds of the invention to form strong complexes with a wide variety of divalent and trivalent metal ions. These organic carbamate compounds exhibit the ability to attach themselves to metal ions to form one or more stable ring structures.

The negative charge of a carbamate anion is distributed over both sulfur atoms which enables the carbamate to be strongly attracted to a metal ion and form a ring structure of the two sulfur atoms with the metal ion. Thus, divalent metal ions will form two stable ring structures or complexes while trivalent metal ions will form three ring structures or complexes with the sulfur atoms, both types of complexes exhibiting strong stability. Complexes formed with monovalent metals such as those which are sodium based are generally water soluble. However, divalent or trivalent metals will displace monovalent metals since the divalent and trivalent complexes formed are larger, more stable, insoluble in water and rapidly precipitate from solution. In the method of the invention, this precipitation process is enhanced by adding polymeric flocculating agents and aggregating agents.

The precipitation of divalent or trivalent metal carbamate complexes occurs over a relatively broad pH range. Most metals will precipitate at neutral pH with a carbamate complex of the invention whereas hydroxide precipitations require a pH greater than 9 for some metals and a pH greater than 10 or 11 for other metals. Generally, removal efficiencies using standard hydroxide precipitation processes degrade with fluctuations of pH whereas the carbamate complexes used are free of this constraint since they are capable of precipitating a wide range of targeted metals at thermal "Removal Efficiency" in the pH range of about 4 to about 10, more typically at neutral pH. Removal Efficiency at a pH of less than about 4 and greater than about 10 is generally on the order of about 50%-60%.

Some of the metallic aqueous waste streams may not be in a proper state of oxidation to be effectively precipitated by the method of the invention. For example, waste streams containing arsenic or chromium may be present as soluble oxanions; i.e., arsenate or chromate. In such instances, a reducing agent can be used to reduce such metals to their trivalent state so that they can be readily precipitated with the carbamate complexes.

#### Continuous Treatment Operation

In continuous treatment, incoming wastes are analyzed and are placed in a tank depending on the level of metal in the waste stream, volume to be handled and the reagents needed to cause metal separation.

Details of the continuous treatment process are as follows:

- a. The waste stream is analyzed.
- b. All incoming waste streams are classified by priority metals.
- c. A solution containing a priority metal of copper, for example, is adjusted to a pH of 6 plus or minus 1 with an acceptable pH variation of plus or minus 1, i.e., a pH range of from about 5 to about 7. The pH is adjusted using NaOH, Ca(OH)<sub>2</sub> or HCL depending on the initial pH of the waste stream.
- d. Once the pH of the waste is adjusted to the desired level, the metal complexing agent of the present invention is added. The waste being treated is allowed to mix with the metal complexing agent for about ten minutes. As above described, the complexing agent preferably comprises about 40% sodium dimethyl-dithiocarbamate, about 10% sodium hydroxide and about 50% water.
- e. After mixing the wastes being treated with the metal complexing agent, calcium chloride solution is added and allowed to mix with the waste for another ten minutes. The amount of calcium chloride added depends on the level of dissolved metals in the solution being treated.
- f. Ferric chloride can be added, as required.
- g. Additional pH adjustment, using sodium hydroxide or calcium hydroxide may be required. The solution is then fed to a flash mix tank at a rate of from about 5 gpm to about 50 gpm, depending on the amount of dissolved and suspended solids where additional calcium chloride and flock are added.

Where the total suspended and dissolved solids are below 0.01% the flow rate could be 50 gpm. This flow rate decreases proportionally as the level of dissolved and suspended solids increases, to where a concentration of 0.5% will require a flow rate of approximately 5 gpm. Flow rates are dependent on the level of dissolved and suspended solids and the type of equipment being used.

h. The solution then travels to the flocculation tank where it is thoroughly mixed allowing particle size growth. The residence time in the flocculation tank is dependent on the level of dissolved solids in the waste solution being treated. The tanks used are sized to allow a minimum of 10 minutes residence time at a flow rate of 50 gpm. For the flocculating reagent to work properly, a minimum residence time of 10 minutes is required in 1,400 gallons for proper mixing and reaction.

i. After the required residence time in the flocculation tank, the waste is fed to a flash mix tank where additional calcium chloride is injected into the waste stream to act as a binder to which the precipitated particles bind and begin to form particles of increasing size.

j. The solution is then passed into a clarification chamber with sufficient surface area to allow the heavy particles to settle to the bottom of the clarification chamber. Clean or clarified solution is removed from the top of the clarification chamber and passing thereafter into a sand filter to remove any small particulate matter that escaped the flocculation and settlement stages and then the effluent goes to a discharge monitoring tank for pH monitoring and discharge.

k. At this point, the solution is fed to the gravity settling tank where the supernatant is separated from the solids. The solids settle to the bottom and are removed to the sludge thickening tank prior to dewatering. The supernatant flows to the filter and finally to discharge. Solid heavy material is removed from the bottom of the settlement chamber periodically. The settlement chamber, or gravity settler tank is one in which clarification of the solution occurs by a process of settlement. The resulting solid or sludge is placed in a sludge thickening tank where it is further settled into a conical shaped bottom of a large holding tank. As solids accumulate at the bottom of this settlement tank, they are drawn off by a

pump and moved into a plate and frame filter press for de-watering. During this operation, excess water is removed from the sludge. The excess water is recirculated back into the treatment system for further use.

l. This process produces an ionic metallic sludge with high metal concentrations without the use of large quantities of reagents such as hydroxides, sodium borohydrate that would be placed in landfill for disposal.

De-watered sludge is removed from the filter press. This material can contain between 25% and 50% moisture by weight. The dewatered sludge or filter cake is placed in infra-red dryers where the moisture content is brought down to less than 20% by weight. The dryers operate at temperatures of between about 350.degree. F. to about 600.degree. F. depending on the metal content and the desired level of moisture for the recovered product.

The resulting volume of recovered metal powder is reduced over the previous de-watering step by as much as 30% to 50% by volume. The drying process drives off the moisture and other compounds that are not metallic leaving the metals in the resulting dry materials heavily concentrated.

m. The recovered dried metal powder is now converted to metallic metal by melting the recovered metal powder in gas-fired or electrical induction melting ovens. The melting process is conducted in two stages and depending on the feed stock, can produce recovered metal ingots of from about 50 to about 90 percent purity.

After de-watering and drying, the recovered metal powder is either sold as a commodity or is further converted to metal ingots. To convert the recovered metal powder to metal, which may be in the form of ingots, the powder is placed into the melting oven where additional reagents are mixed with the recovered metal powder. The reagents added are sodium tetra borate pentahydrate and soda ash.

Sodium tetra borate pentahydrate is added to the powder to cause the metals to liquefy once they reach the melting point. Soda ash is used to cause the metal to separate from the flux. Flux is the combination of the soda ash and sodium tetra borate pentahydrate (borax) used during the melting process.

The powder is first mixed with sodium tetra borate pentahydrate and melted to cause a reduction in volume and produce a homogenous mixture of metal and borax. This mixture is poured, cooled and re-melted in a second melting oven where soda ash is added to cause separation in the melted state. This material is poured and allowed to cool.

Once cooled, the recovered metal, which has settled to the bottom of the mold is separated from the slag comprised of the flux layer that is on top of the recovered metal. The slag is reused in the next melt.

For those melts that produce clean black slag, the black slag is sold as a cleaning compound. For those melts that produce a semi pure slag, the slag is sold along with the metal to a primary smelter purchasing the recovered metal.

The temperature in the melting oven is brought up to approximately 1800.degree. F. and the materials are allowed to melt until it is verified that all the material in the crucible is liquid. This usually takes from 2-4 hours depending on the temperature of the oven when it is first charged. For example, a melt from a cold oven will take about 4 hours, whereas a melt from a hot oven will usually take about 2 hours. At this point, the molten materials are poured into a cast iron buggy or mold that has been pre-heated and coated with carbon to prevent the molten material from sticking to the buggy walls. The purpose of the preheating is to drive out any residual moisture and ensure that the surface is not cold



when pouring in the molten bath. If the mold were cold, it might break from the sudden heat change or it might cause the molten bath to spray molten slag out of the mold.

The material is allowed to cool and solidify at which time the resulting solid is removed from the buggy and separated in two different layers. The material is then placed into a second melting oven where the temperature is brought up to approximately 1800.degree. and two additional reagents are added, to induce the material to separate into three layers.

The lower layer consists of 60% to 90% of the recovered metal such as copper or nickel. The second or middle layer consists of pig iron containing all of the remaining metals, and the top layer consists of slag, i.e., the flux containing the two reagents that were added, one to each melt. The resulting products from this operation are solid and are commercially recycled thus completing the recycling of the components in the wastes. These materials can then be sold as feed stock for primary smelting operations.

The above noted procedures to produce recovered metal ingot are representative of each time the sludge is removed from the filter process. The amount of sludge removed is directly related to the amount of dissolved salts in the waste at the beginning of the metal recovery process. For example, a solution containing 1 pound of dissolved salts produces approximately 1 pound of sludge.

#### Batch Treatment

Batch treatment takes place in one of a number of different tanks and is a process that may be completed in the starting tank. A cycle of operations is completed, and the effluent is removed for discharge, while the metal recovery products are either removed or utilized for future batch processes, and the cycle is repeated.

This batch recovery method is used for solutions containing precious metals above 250 mg/liter and for non-precious metal solutions containing concentrations of a priority metal above 0.2% (2,000 mg/liter).

In the batch process, one cycle of operations is completed and the effluent is removed for discharge to the sewer while the metal recovery products are either removed or utilized for future batch process and the cycle is repeated.

Upon completion of analysis and selective separation of priority metals by the aforementioned processes, wastes containing precious metals are treated, as follows:

- a. All wastes containing precious metal with low chromium content, generally less than 10 ppm of chromium, are placed in a separate tank dedicated to such wastes and are subjected to batch treatment operations.
- b. Chromium present in wastes at levels greater than approximately 10 ppm interferes with removal of other metals from solution. When the chromium concentration of waste to be treated is generally greater than about 10 ppm, the waste must be separated from other waste treatment. All wastes containing precious metals with high chromium content are placed in a separate batch treatment tank to undergo batch treatment for high chromium and precious metals. The high chromium waste is then separately treated as elsewhere described herein.

#### EXAMPLES

The following illustrative examples are set forth to demonstrate the utility of the present invention of a

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number of different waste streams.

### Example 1

Example 1 illustrates treatment of a solution containing cyanide and metals in concentrations more than 500 mg/liter.

Large volumes are handled in an appropriate size tank. The waste is transferred to the treatment tank using an air activated diaphragm pump. The waste is then tested for pH and Oxygen Reduction Potential (ORP).

The solution is maintained at a pH above 10.5 with the addition of caustic while the cyanide is oxidized using oxidizing reagents to maintain an alkaline state within the solution. When the solution reaches and maintains the desired ORP for the desired length of time, a sample is taken and analyzed for cyanide content. This method controls the generation of heat and prevents uncontrolled chemical reactions. When all the cyanide has been oxidized and the batch is low enough in metal content, any remaining wastes are integrated into the regular treatment for metal recovery.

If the metal level is above 1000 mg/liter, the batch will be completed in the same treatment tank. If the metal level is less than 1000 mg/liter, the solution is fed into a continuous treatment operation containing the same priority metal.

All unused oxidizer is driven off from the solution by reducing the pH to a point where the oxidizer will be liberated as a gas. The liberated gas is trapped by an air scrubbing system attached to the treatment tanks and neutralized prior to being discharged to the atmosphere. This prevents the oxidizer from neutralizing the metal complexing agents that will be added to the solution during this operation.

The ionic metal will drop out of the solution and become particulate matter. To increase the rate of settlement, the pH of the solution will be adjusted to an ideal point of insolubility for the priority metal and a bindery agent such as calcium chloride will be added.

The solution is allowed to mix for a predetermined time at which point a polymer is added to cause the particles to increase in size. At this point, mixing is terminated and the solution is allowed to settle. The clean effluent or supernatant is removed for monitoring and discharge, while the ionic metal sludge that settled to the bottom of the tank is removed and placed in the sludge thickening tank prior to dewatering, drying and melting. Table I illustrates details regarding quantities of reagents added:

TABLE I			
Treatment Reagents for Example 1			
Step	Operation	Reagent	Quantity
1	100 gallons	H.sub.2 O	3:1
2	pH to 8	Ca(OH).sub.2	30 gr.
3	Complexing Agent	Na.sub.2 S	1 gal.
4	Complexing Agent	*	0.5 gal.
5	pH 9.5	Ca(OH).sub.2	3 gr.

### Elemental Analysis of Example 1 Metals

Element	Amount	Measurement Procedure
		(United States Government)

Arsenic	<0.050	SW-846 6010 ICP
Aluminum	2362.000	SW-846 6010 ICP
Barium	68.690	SW-846 6010 ICP
Beryllium	<0.001	SW-846 6010 ICP
Cadmium	0.010	SW-846 6010 ICP
Hexavalent Chromium	<0.001	SM17-418.1 UV
Copper	418.000	SW-846 6010 ICP
Iron	203.400	SW-846 6010 ICP
Lead	3.280	SW-846 6010 ICP
Manganese	1.030	SW-846 6010 ICP
Mercury	0.073	SW-846 7470 AA
Nickel	0.500	SW-846 6010 ICP
Phenol	<0.020	SW-846 9065 UV
Selenium	<0.050	SW-846 6010 ICP
Silver	9.480	SW-846 6010 ICP
Zinc	0.620	SW-846 6010 ICP

### The Physical Analysis of Example 1 is

Physical Attributes	Results	Measurement Procedure (United States Government)
Color	Dark Brown	
Cyanide	<0.02	SW-846 9010
Flash Point	>200.degree. F.	SW-846 1010
Odor	None	
pH	-0.21	SW-846 9040
Percent Solids	<1%	SM17 2540b & 2540D
Specific Gravity	1.02	
Total Petroleum	NA	SM17 418.1
Hydrocarbons		
Viscosity	Medium	
Layers When Standing	1	
Percent Moisture	NA	

### Example 2

In this example, a metal waste stream containing hexavalent chromium is treated. The pH of the solution is reduced to less than 2.0. A reducing agent such as sodium meta-bisulfate is added and allowed to react with the waste for approximate 20 minutes to ensure complete contact and reduction of the hexavalent chromium to trivalent chromium.

The pH of the solution is adjusted to 3.5 and a volume of the metal complexing agent will be added. The pH will rise with this addition and the ionic metal will drop out of the solution and become particulate matter. To increase the rate of settlement, the pH of the solution will be adjusted to the ideal point of insolubility for the priority metal and a bindery agent such as calcium chloride will be added.

The solution will be allowed to mix for a predetermined time at which point a flocculating agent will be added to cause the particles to increase in size. Mixing will be terminated, and the solution will be allowed to settle. The clean effluent or supernatant will be removed for monitoring and discharged to the sewer while the ionic metal sludge that settled to the bottom of the tank will be removed and placed in

the sludge thickening tank prior to de-watering, drying and melting.

Table II below sets forth the details of the reagents used:

TABLE II			
Treatment Reagents for Example 2			
Step	Operation	Reagent	Quantity
1	100 gallons	H.sub.2 O	10:1
2	Reduce	NaHSO.sub.3	25 lbs./100 gal. of wastes
3	pH 7.00	CaOH.sub.2	60 lbs/100 gal. of waste
4	Complexing Agent	Na.sub.2 S	0.2 lbs./1000 gal. of waste
5	Complexing Agent	*	0.2 gal./1000 gal. of waste
6	Coagulant 1	CaCl.sub.2	5 gal./100 gal. of waste
7	Coagulant 2	Flocculating Agent	1/4 lbs. per 100 gal.

\*40% sodium dimethyl-dithiocarbamate, 10% sodium hydroxide and 50% water

### Elemental Analysis of Example 2 Metals

Element	Results	Measurement Procedure (United States Government)
Arsenic	20.00	SW-846 6010 ICP
Aluminum	7232.00	SW-846 6010 JCP
Barium	<0.01	SW-846 6010 ICP
Beryllium	5.30	SW-846 6010 ICP
Cadmium	108.60	SW-846 6010 ICP
Chromium	32070.00	
Hexavalent Chromium	146.60	SM17-418.1 UV
Copper	146.60	SW-846 6010 ICP
Iron	685.70	SW-846 6010 ICP
Lead	<0.01	SW-846 6010 ICP
Manganese	22.3	SW-846 6010 ICP
Mercury		SW-846 7470 AA
Nickel	340.90	SW-846 6010 ICP
Phenol		SW-846 9065 UV
Selenium	<0.05	SW-846 6010 ICP
Silver	74.10	SW-846 6010 ICP
Zinc	393.30	SW-846 6010 ICP

### The Physical Analysis of Example 2 is

Physical Attributes	Results	Measurement Procedure (United States Government)
Color	Dark Brown	
Cyanide	<0.02	SW-8469010
Flash Point	>200.degree. F.	SW-846 1010
Odor	None	
pH	-0.21	SW-846 9040
Percent Solids	<1%	SM17 2540b & 2540D
Specific Gravity	1.02	
Total Petroleum	NA	SM17 418.1
Hydrocarbons		
Viscosity	Medium	

Layers When	1
Standing	
Percent Moisture	NA

### Example 3

This example describes the treatment process of a precious metal bearing solution containing chromium.

The pH of the solution is reduced to less than 2.0 with the addition of hydrochloric acid (HCl). A reducing agent such as sodium meta-bisulfate is added to reduce the chromium. The solution is then agitated for approximately 20 minutes to ensure complete contact and reduction of the chromium.

The pH of the solution is then increased to greater than 10.5 with the addition of caustic reagents and a quantity of sodium hypochlorite is added to oxidize any remaining chelating reagents. The oxidizer is added in small quantities to prevent over feeding.

The pH is allowed to stabilize for approximately 15 minutes and is then adjusted to a pH of 7.5, as necessary. If the pH drifts, additional pH stabilization is implemented.

Metal complexing reagents are added to the solution in sufficient quantity to cause all of the dissolved metal to precipitate out of the solution.

After the desired settlement time, the solution is checked for metal content. Upon completion of the settlement process, the clean effluent is removed for monitoring prior to discharge, and the ionic metal sludge is removed to a conical-bottomed sludge thickening tank prior to de-watering and drying.

When the sludge is transferred from the treatment tank to the conical-bottomed sludge thickening tank, a portion of the liquid is also transferred, in order to facilitate the transfer. Allowing separation of sludge from transfer liquid in the conical-bottomed thickening tank is simply called "sludge thickening" and the tank in which it is accomplished is so named.

### Example 4

This example relates to a precious metal bearing solution (such as photographic processing waste) without chromium. Recovery of the metals from this type of solution is conducted in a batch operation for control over the recovered product, reuse of the recovered product as a seed for the next operation, cost of the complexing agent, keeping the solution from outside contaminants and complying with regulations that exempt precious metal recovery.

All material is placed in a large common holding tank. In this case, the tank has a capacity of 7,000 gallons, is closed topped and vented to the atmosphere through a permitted air scrubber. Once a sufficient quantity of material is placed in the holding tank, samples are obtained from the top and bottom of the tank. These samples are analyzed for metal content.

A bindery agent such as calcium chloride is mixed by dissolving approximately 50 pounds of it in 100 gallons of water and the resulting solution is fed into the holding tank by pumping it in through the bottom of the tank so as to ensure mixing and adequate contact with the solution in the holding tank.

Based on the metal content, i.e., the concentration of suspended and dissolved metals determined to be present in the solution by chemical analysis, the metal complexing agent is fed into the holding tank by being pumped in from the bottom to ensure adequate contact with the solution in the tank. The amount of complexing and bindery agents added to the batch is directly related to the level of metal in the batch. For example, a 7,000 gallon batch containing 3,000 mg/liter of dissolved metal requires approximately 12 gallons of metal complexing agent and 100 gallons of bindery agent to bring the metal levels to below 2 mg/liter of combined metals. The tank is agitated from the bottom with air from an air pump for approximately 30 minutes to ensure adequate mixing of the bindery agent, metal complexing agent and the solution in the tank. The contents of the tank are then allowed to settle for approximately three to six hours, after which time samples are obtained from the top and bottom of the tank for chemical analysis. Alternatively, the metal complexing agent can be added to the tank by itself to cause the separation and in such a case, CaCl.sub.2 is not used.

Based on the analytical results which, under normal operating conditions shows that the solution is clean, the clean effluent is removed by use of an electric centrifugal pump for pH monitoring prior to discharge. Monitoring occurs in a discharge holding tank just prior to sewer discharge.

The precipitated metal sludge is allowed to remain at the bottom of the tank as a seed for the next batch to be processed in this tank. Under normal conditions, this seed remains for five to six cycles before it is removed and the cycle is started over.

When the metal sludge generated in this batch operation is removed from the processing tank, the sludge is placed into fifty-five gallon holding drums for storage prior to being processed in a dedicated filter press. Effluent from the filter press operation is returned to the dedicated batch process tank and reused.

De-watered solids from this operation are placed directly into a silicon carbide crucible in a melting oven, where the solids are blended with a flux, i.e., sodium borate tetra pentahydrate and soda ash. For each 40 pounds of recovered product that is placed in the first oven for stage one of the melting process, approximately three pounds of sodium tetra borate pentahydrate are added. For each melt in stage two of the melting process, approximately 9-12 pounds of soda ash are added.

The melting oven is brought up to approximately 1800.degree. F. and monitored. Once it is determined that the batch is in a homogenous liquid state by stirring, the contents of the crucible are poured into a cast iron buggy (mold) that has been pre-heated and coated with a carbon water solution to prevent sticking of the molten material. The mold is allowed to cool for 18 hours and the contents are removed and separated into three components.

Noble metal (usually 95% or higher concentration silver), pig iron and slag is recovered. Both the silver and pig iron are placed into a second melting oven where additional soda ash is added and the oven is brought to approximately 1800.degree. F. Once it is determined that the batch is molten by stirring the bath, approximately one pound of black iron is added to the molten bath and allowed to completely melt. The bath is then stirred to verify that the black iron has melted.

After stirring is completed, the molten bath is poured into a pre-heated buggy (mold) that has been coated with carbon black to prevent the molten material from sticking to the sides of the mold. The mold is allowed to cool for approximately 14 hours at which time the mold is emptied.

The recovered products are removed from the mold and separated into three layers consisting of a noble metal such as silver with a purity of from 97% to 99.9%, a layer of pig iron containing all of the impurities, i.e., aluminum, cadmium, chromium, cobalt, copper, iron, manganese, nickel and zinc), and a layer of black slag.

The black slag is recycled two to three times in the same operation before it is sold as a scrubbing compound. The pig iron and silver are both sold for their metal content completely recycling all of the components within the incoming waste that caused the material to be classified as waste.

Table III below sets forth the percentage of recovery for those metals analyzed in the incoming waste of Example 4.

TABLE III

ELEMENT	INCOMING WASTE	SUPERNATANT	
		AFTER RECOVERY	PERCENTAGE OF RECOVERY
Arsenic	<0.050	<0.050	0.000%
Antimony	<0.050	<0.050	0.000%
Aluminum	248.400	1.773	99.287%
Barium	<0.001	<0.001	0.000%
Beryllium	<0.001	<0.001	0.000%
Calcium	385.500	265.300	31.258%
Cadmium	1.560	<0.002	99.872%
Chromium	0.230	<0.005	97.826%
Cobalt	1.160	<0.003	99.741%
Copper	167.900	<0.002	99.999%
Iron	762.700	<0.005	99.993%
Lead	<0.025	<0.025	60.000%
Magnesium	396.500	17.540	95.576%
Manganese	161.900	0.250	99.846%
Mercury	<0.020	<0.020	0.000%
Nickel	1.310	<0.010	99.237%
Phenol	<0.020	<0.020	0.000%
Potassium	16.340	8.230	49.633%
Selenium	0.060	<0.050	16.667%
Silver	0.010	<0.003	70.000%
Sulfate	8596.000	3400.000	60.447%
Thallium	0.800	<0.020	82.500%
Vanadium	0.470	<0.020	95.745%
Zinc	570.000	<0.004	99.993%

### Example 5

This example illustrates application of the method of the invention to recover metals and compounds from the liquid waste streams of abandoned or existing mines as well as operating and active mines and other ore extraction processes.

Using an appropriate extraction system such as pumps, the liquid mine waste or process effluent from a mine is fed to a facility that treats the liquid mine waste or process effluent with a method of the invention; i.e., either the continuous or the batch method. The resulting clean effluent can then be reused in the mining process or discharged into the ground water table or a sewage system or introduced into a potable water distribution system.

Thus, operating and active mines can increase the efficiency of their ore extraction processes by incorporating the method of the invention directly into the mining process to realize a greater percent of removal of metals from the virgin ore materials.

The metals and other compounds that can be recovered are shown in Table IV below.

TABLE IV COMPOUNDS/ METALS	INFLUENT (ppm)	EFFLUENT (ppm)
Arsenic	0.648	<0.050
Antimony	0.050	<0.050
Aluminum	310.500	1.773
Barium	0.101	<0.001
Beryllium	0.072	<0.001
Calcium	385.500	265.300
Cadmium	1.693	<0.002
Chromium (Total)	0.001	<0.005
Cobalt	1.160	<0.003
Copper	204.600	<0.002
Iron	1053.000	<0.005
Lead	0.071	<0.025
Magnesium	396.500	17.540
Manganese	176.100	<0.250
Mercury	<0.020	<0.020
Nickel	0.685	<0.010
Phenol	<0.020	<0.020
Potassium	16.340	8.230
Selenium	0.253	<0.050
Silver	0.133	<0.003
Sulfate	8596.000	3400.000
Thallium	0.800	<0.020
Vanadium	0.470	<0.020
Zinc	649.100	<0.004

#### Example 6

This example illustrates the application of the method of the invention to recover metals and compounds from contaminated groundwater.

Depending upon the subsurface hydro geologic conditions, including the nature of the hydraulic gradient across the contaminated plume to be treated, a system of deep well and shallow well points is created downstream or down gradient from the source of contamination and completely intercept the contaminated plume. Any insoluble or volatile organic matter is first segregated and removed from the contaminated groundwater using conventional screening and settling techniques. The contaminated groundwater is then fed to a facility containing either the continuous or batch method of the invention for removal and recovery of metals and other compounds from the contaminated groundwater to recover clean, uncontaminated water which can then be further processed for use as potable water. The clean, uncontaminated water can also be delivered to a well at the foot of the system to form a pressure ridge that facilitates the formation of an upcoming effect in the water table and thus prevents the contaminated plume from migrating past the system treatment area. The metals and other compounds recovered can be separated and refined using conventional methods.

Table V below illustrates the metals and other compounds that can be recovered using this method.

TABLE V COM- POUNDS/ INFLUENT	EFF- LUENT	RECOVERED MATERIAL	PERCENT OF RECOVERY
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METALS	(ppm)	(ppm)	(ppm)	(%)
Arsenic	<0.050	<0.050	<0.050	0.000*
Antimony	<0.050	<0.050	<0.050	0.000*
Aluminum	1238.000	5.536	46,690.000	99.553
Barium	0.027	0.001	6.720	96.296
Beryllium	0.045	<0.001	2.575	100.000
Calcium	405.500	694.100	162,100.000	71.171#
Cadmium	0.941	<0.002	42.580	100.000
Chromium	32.970	0.030	1,613.000	99.909
Cobalt	3.510	0.185	131.100	94.729
Copper	3.680	0.040	158.900	98.913
Iron	378.000	0.126	13,600.000	99.967
Lead	<0.025	<0.025	<0.025	0.000
Magnesium	1,193.000	115.100	38,600.000	90.352
Manganese	174.800	0.256	7,103.000	99.854
Nickel	6.700	0.015	323.600	99.716
Selenium	<0.050	<0.059	8.360	0.000
Silver	0.106	<0.003	14.670	100.000
Thallium	<0.050	<0.020	<0.020	0.000
Vanadium	0.822	<0.020	35.960	100.000
Zinc	17.400	0.013	802.200	99.925

### Example 7

This example illustrates the use of the method of the invention to obtain potable water.

Using conventional techniques, the water intended for potable use is first treated to remove or segregate insoluble and volatile organic matter. Nitrates are then removed from the water and ionic aluminum or ionic iron is then added to improve color, reduce turbidity and destroy bacteria.

The thusly treated water is then fed to a facility of the invention; i.e., either the continuous or the batch method, to remove metals and other compounds as a sludge, if necessary, and the effluent is treated with lime-soda or subjected to ionic exchange treatment or further treated with a method of the invention to remove excess calcium and magnesium to a desired level of from about 75 to about 120 mg/l calcium carbonate level.

The effluent is then filtered using conventional methods such as granulated active carbon to remove residual particulate matter and offensive tastes or odors. The effluent is then disinfected by chlorination using such compounds as chlorine, sodium per chlorate, calcium per chlorate, and the like, to reduce pathogens to an acceptable level.

The effluent is then ready to be incorporated into a potable water distribution system while the sludge is treated according to the method of the invention to recover commercial grade metals.

### Example 8

This example illustrates the use of the batch method of the invention as an in situ application to remove metals and other compounds from standing, contaminated water such as from ponds, lagoons, pits, and the like.

A physical and chemical analysis of the contaminated water is first ascertained and the specific hydraulic, geophysical and geochemical conditions of the contaminated water are determined.



Concurrently with or subsequent to mixing, the reagents of the batch method of the invention are then introduced into the in situ contaminated water and permitted to react for a period of time sufficient for the metals and other compounds to aggregate and settle as a sludge at the bottom of the standing water. Using conventional pumps, the sludge is then extracted and dried and the metals recovered in commercial grade as described hereinabove. The cleaned water can then be left standing, be reused as process water, be discharged into the ground, be discharged into the sewerage system, or be introduced into a potable water distribution system.

#### Example 9

This example illustrates the application of a method of the invention to treat waste streams containing more than 2% by weight solids in solution by introducing the metals contained in the waste streams into a liquid solution from which the metals can then be remediated, recovered and separated.

In this method, the waste stream to be treated is first isolated or diverted and insoluble and volatile organic matter is removed using conventional techniques. The resultant solid waste is then washed with water or exposed to an acid matrix until a homogeneous solution.

The homogeneous solution is then fed to a facility and subjected to either the continuous or the batch method of the invention to recover metals of commercial quality while the resultant effluent can be discharged into the ground, or into a sewerage system, or introduced into a potable water distribution system.

#### Example 10

This example illustrates the application of the method of the invention in conjunction with a conventional, commercial air scrubber to remove and recover metals from polluted or contaminated air.

As desired or required, the incoming air to be treated can be filtered before being fed into the scrubber. The scrubber used is typically a wet collector scrubber; e.g., a venturi-cyclone type, which is capable of enabling the reagents used in the method of the invention to contact the polluted or contaminated air either in the form of an aqueous solution or as an aerosol spray. Thus, the invention reagents are introduced into the scrubber effluent to remain in contact with the contaminated or polluted air for a time sufficient for the metals and other compounds to be removed to aggregate and fall to the bottom of the scrubber in the form of a sludge. The sludge is then removed from the scrubber, dried and treated as described hereinabove to recover metals of commercial quality while the resultant clean effluent can be discharged into the ground or into a sewerage system or introduced into a potable water distribution system.

#### Example 11

This example illustrates use of the method of the invention to recover electroless nickel and electroless copper used in conventional plating processes.

The waste stream to be treated is fed to a facility and subjected to either the continuous or batch method of the invention which is adapted to recover electroless nickel or electroless copper. For the recovery of electroless nickel or electroless copper, the pH of the waste stream is adjusted to from about 6.0 to about 8.5 and then reduces with sodium sulfate and ferrous sulfate. Calcium chloride is then added as an aggregating agent followed by the addition of a complexing agent such as sodium dimethyldithiocarbamate, a precipitating agent such as trimercapto-s-triazine or trisodium salt, and a flocculent to form a sludge. The metals, i.e., nickel or copper, are then recovered from the sludge as

described hereinabove.

#### Example 12

This example illustrates the application of the invention to recover low level radioactive metals from waste streams.

The waste stream containing the low level radioactive metals are delivered to a chamber where the waste stream is subjected to either the continuous or the batch method of the invention and recovery of the metals from the resultant sludge is as described hereinabove. Accordingly, recovery of such low level radioactive metals a cesium strontium, thorium and radium can be realized in amounts greater than about 50% while recovery of low level radioactive metals such as uranium, plutonium, americium, neptunium and cobalt can be realized in amounts greater than about 95%. In addition, recovery of such metals as nickel, lead, iron, silver and chromium can also be realized in amounts greater than about 95%.

#### Example 13

This example Illustrates the use of the method of the invention for fixating, removing, separating and recovering metals from solid and soil wastes.

If required, the contaminated soils or solids are extracted from their residence and then mixed with a liquid or powder containing a high concentration of the reagents used in the batch method of the invention. After thorough mixing, the metals become fixated and entrained in the solids or soil and are analogous to ore materials extracted from the ground. The solids or soil containing the fixated metals can then be subjected to an extraction process to remove the metals and the cleaned solids or soil can be returned to the ground while the extracted metals can be subjected to primary or secondary smelting operations to recover the metals.

#### Example 14

This example illustrates the method of the invention to recover metals and compounds from steel manufacturing wastewater. In this example, preparatory treatment included adding potassium permanganate as an oxidizer and separation included the use of sodium dimethylethiocarbamate as a complexing agent and a polymeric flocculating agent prior to dewatering. The results obtained are shown in Table VI below.

TABLE VI

ELEMENT	INFLUENT (ppm)	EFFLUENT (ppm)
Arsenic	<0.014	<0.014
Aluminum	<0.002	<0.002
Barium	0.144	0.135
Boryllium	0.000	0.000
Cadmium	<0.001	<0.001
Chromium	<0.002	<0.002
Copper	<0.005	<0.005
Iron	22.910	0.018
Lead	<0.014	<0.014
Manganese	0.330	0.235
Mercury	0.490	<0.001
Nickel	<0.003	<0.003
Selenium	<0.018	<0.018
Silver	<0.002	<0.002
Zinc	0.094	<0.001

### Example 15

This example illustrates the method of the invention to recover metals and compounds from battery manufacturing or chemical manufacturing wastewater. In this example, preparatory treatment included adding lime to adjust the pH to from about 4.5-5.5 and adding aluminum sulfate as an ion exchange promoter. For separation, sodium dimethyldithiocarbamate was used as the complexing agent and a polymeric flocculating agent was added prior to dewatering. The results obtained are shown in Table VII below.

TABLE VII

ELEMENT	INFLUENT (ppm)	EFFLUENT (PPM)
Arsenic	<0.002	<0.002
Antimony	0.247	<0.005
Aluminum	0.393	5.307
Barium	0.055	0.058
Beryllium	0.000	0.000
Calcium	108.200	146.300
Cadmium	0.224	0.003
Chromium	0.044	<0.002
Cobalt	0.100	<0.001
Copper	0.048	<0.005
Iron	0.710	0.072
Lead	0.899	0.018
Magnesium	22.760	4.420
Manganese	0.165	0.011
Nickel	0.242	<0.003
Selenium	0.215	0.132
Silver	<0.002	<0.002
Thallium	0.106	0.023
Vanadium	0.047	<0.001
Zinc	2.270	<0.001

### Example 16

This example illustrates the method of the invention to recover metals and compounds from wastewater resulting from printed circuit board manufacturing. In this example, preparatory treatment included adding lime to adjust the pH to from about 7.5-8.5 and adding calcium chloride as an aggregating agent. Separation included the use of sodium dimethyldithiocarbamate as a complexing agent and adding a polymeric flocculating agent prior to dewatering. The results obtained are shown in Table VIII below.

TABLE VIII

ELEMENT	INFLUENT (ppm)	EFFLUENT (ppm)
Arsenic	<0.014	<0.014
Aluminum	30.10	0.501
Barium	0.107	<0.001
Beryllium	<0.001	<0.001
Cadmium	0.060	<0.001
Chromium	2.290	<0.002
Copper	6026.00	0.075
Iron	404.30	1.398

Lead	83.49	<0.014
Manganese	43.45	2.134
Mercury	<0.00	<0.002
Nickel	0.92	<0.003
Selenium	1.94	<0.018
Silver	3.65	<0.002
Zinc	<0.001	<0.001

### Example 17

This example illustrates the method of the invention to recover metals and compounds from titanium pickle wastewater. In this example, preparatory treatment included adding lime to adjust the pH to from about 6.5-8.0 and calcium chloride as an aggregating agent. Separation included the use of either dimethyldithiocarbamate and/or sodium sulfide and/or a polythiocarbonate as a complexing agent and the addition of a polymeric flocculent prior to dewatering. The results obtained are shown in Table IX below.

TABLE IX

ELEMENT	INFLUENT (ppm)	EFFLUENT (ppm)
Arsenic	8.61	<0.014
Aluminum	1470.00	1.252
Barium	1.82	<0.001
Beryllium	22.58	<0.001
Calcium	<0.001	<0.001
Chromium (Total)	208.40	<0.002
Copper	64.50	<0.005
Iron	383.80	6.521
Lead	1900.00	0.071
Manganese	24.17	0.872
Mercury	0.05	<0.002
Nickel	501.20	0.531
Selenium	<0.018	<0.018
Silver	<0.002	<0.002
Titanium	75,000.00	3.181
Zinc	146.30	<0.001

### Example 18

This example illustrates the method of the invention to recover metals and compounds from nickel plating waste water. In this example, preparatory treatment included adding lime to adjust the pH to from about 5.5-7.5, adding calcium chloride as an aggregating agent and adding aluminum sulfate as an ion exchange promoter. Separation included the use of sodium dimethyldithiocarbamate as a complexing agent and the addition of a polymeric flocculating agent prior to drying. The results obtained are shown in Table X below.

TABLE X

ELEMENT	INFLUENT (ppm)	EFFLUENT (ppm)
Arsenic	<0.014	<0.014
Aluminum	<0.002	<0.002

Barium	<0.001	<0.001
Beryllium	<0.001	<0.001
Cadmium	0.535	<0.001
Chromium	0.040	<0.00
Copper	3.114	<0.005
Iron	103.40	<0.002
Lead	5.440	<0.014
Manganese	0.001	<0.001
Mercury	<0.002	<0.002
Nickel	21,610.00	0.991
Selenium	<0.018	<0.018
Silver	<0.002	<0.002
Zinc	17,120.00	0.236

### Example 19

This example illustrates the method of the invention to recover metals and compounds from wastewater resulting from chrome plating processes. In this example, preparatory treatment included adding lime to adjust the pH to from about 5.5-7.5, adding sodium mteabisulfate as an oxidizer and adding calcium chloride as an aggregating agent. Separation included the use of sodium dimethyldithiocarbamate as a complexing agent and a polymeric flocculent prior to dewatering. The results obtained are shown in Table XI below.

TABLE XI		
ELEMENT	INFLUENT (ppm)	EFFLUENT (ppm)
Arsenic	6.19	<0.014
Aluminum	65.83	<0.002
Barium	639.10	<0.001
Beryllium	156.80	<0.001
Cadmium	7.25	<0.001
Chromium (Total)	202,200.00	2.178
Copper	7616.00	0.861
Iron	19,120.00	0.034
Lead	72,890.00	0.009
Manganese	83.19	<0.001
Mercury	<0.002	<0.002
Nickel	2443.00	1.561
Selenium	<0.018	<0.018
Silver	<0.003	<0.002
Zinc	17,120.00	1.671

### Example 20

This example illustrates the method of the invention to recover metals and compounds from the wastewater resulting from electroless nickel operations. In this example, preparatory treatment included the use of calcium chloride as an aggregating agent and ferrous sulfate as an ion exchange agent. Separation included the use of sodium dimethyldithiocarbamate as a complexing agent and/or a polymeric flocculent prior to dewatering. The results obtained are shown in Table XII below.

TABLE XII		
	INFLUENT	EFFLUENT

ELEMENT	(ppm)	(ppm)
Arsenic	<0.014	<0.014
Aluminum	<0.002	<0.002
Barium	0.086	<0.001
Beryllium	<0.001	<0.001
Cadmium	0.458	<0.001
Chromium	2.016	0.005
Copper	15.010	0.007
Iron	<0.002	<0.002
Lead	0.592	<0.014
Manganese	<0.001	<0.001
Mercury	<0.002	<0.002
Nickel	6190.00	0.679
Selenium	<0.018	<0.018
Silver	<0.002	<0.002
Zinc	32.540	0.009

### Example 21

This example illustrates the method of the invention to recover metals and compounds from X-ray and photographic waste waters. In this example, separation included the use of sodium dimethyldithiocarbamate as a complexing agent. The results obtained are shown in Table XIII below.

TABLE XIII

ELEMENT	INFLUENT (ppm)	EFFLUENT (ppm)
Arsenic	0.06	<0.014
Aluminum	200.70	1.235
Barium	0.03	<0.001
Beryllium	<0.001	<0.001
Cadmium	0.05	<0.001
Chromium (Total)	0.21	<0.002
Copper	0.23	<0.005
Iron	2.26	0.004
Lead	0.19	<0.014
Manganese	0.03	<0.001
Mercury	<0.002	<0.002
Nickel	0.06	<0.003
Selenium	0.08	<0.018
Silver	853.70	<0.002
Zinc	1.56	<0.001

### Example 22

This example illustrates the method of the invention to recover metals and compounds from wastewater resulting from aluminum anodizing operations. In this example, preparatory treatment included the use of calcium chloride as an aggregating agent and separation included the use of sodium dimethyldithiocarbamate as a complexing agent and/or a polymeric flocculent prior to dewatering. The results obtained are shown in Table XIV below.

TABLE XIV

INFLUENT	EFFLUENT
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ELEMENT	(ppm)	(ppm)
Arsenic	<0.014	<0.014
Aluminum	34,810.00	2.634
Barium	2.01	<0.001
Beryllium	0.33	<0.001
Cadmium	55.71	<0.001
Chromium	305.10	<0.002
Copper	18,370.00	0.089
Iron	16,380.00	0.067
Lead	246.00	0.090
Manganese	853.00	0.175
Mercury	<0.002	<0.002
Nickel	333.90	0.112
Selenium	<0.018	<0.018
Silver	<0.002	<0.002
Zinc	13,490.00	0.879

### Example 23

This example illustrates the method of the invention to recover metals and compounds from wastewater resulting from construction and demolition landfill leaches. During separation in this example, sodium dimethyldithiocarbamate was used as a complexing agent prior to dewatering. The results obtained are shown in Table XV below.

TABLE XV		
ELEMENT	INFLUENT (ppm)	EFFLUENT (ppm)
Arsenic	0.060	<0.014
Aluminum	0.113	<0.002
Barium	0.030	<0.001
Beryllium	0.010	<0.001
Cadmium	0.015	<0.001
Chromium (Total)	0.021	<0.002
Copper	<0.005	<0.005
Iron	1.262	<0.002
Lead	0.019	<0.014
Manganese	0.003	<0.001
Mercury	<0.002	<0.002
Nickel	0.006	<0.003
Selenium	0.111	<0.018
Silver	<0.002	<0.00
Zinc	<0.001	<0.001

### Example 24

This example illustrates the method of the invention to recover metals and sulfates from waste streams. In this example, preparatory treatment included adjusting the pH with an acid to no greater than 4.0. During separation, a complexing agent comprising a mixture of barium carbonate and sodium dimethyldithiocarbamate was added and the pH was then adjusted with a base to 7.0. Prior to dewatering, a polymeric flocculating agent was added. The results obtained are shown in Table XVI below.

TABLE XVI

ELEMENT	INFLUENT (ppm)	EFFLUENT (ppm)
Arsenic	<0.002	<0.002
Antimony	0.247	<0.005
Aluminum	0.393	5.307
Barium	0.055	0.058
Beryllium	0.000	0.000
Calcium	108.200	146.300
Cadmium	0.224	0.003
Chromium	0.044	<0.002
Cobalt	0.100	<0.001
Copper	0.048	<0.005
Iron	0.710	0.072
Lead	0.899	0.018
Magnesium	22.760	4.420
Manganese	0.165	0.011
Nickel	0.242	<0.003
Selenium	0.215	0.132
Silver	<0.002	<0.002
Sulfates	3000.000	<1.000
Thallium	0.106	0.023
Vanadium	0.047	<0.001
Zinc	2.270	<0.001

**Example 25**

This example illustrates the use of the method of the invention to selectively recover cadmium and lead from highly acidic waste streams or other process liquids having a high acidic content without adjusting the pH of the waste stream or process liquid. In this example, sodium dimethyldithiocarbamate was used as the complexing agent to treat a phosphoric acid liquid waste stream resulting from the manufacture of fertilizers and having a pH of 0.38. During treatment, the pH was not further adjusted or manipulated. The results obtained are set forth in Table XVII below.

TABLE XVII

ELEMENT	INFLUENT (ppm)	EFFLUENT (ppm)
Aluminum	4496.00	3665.00
Arsenic	13.79	6.26
Cadmium	154.10	6.16
Chromium	555.40	378.90
Lead	55.91	2.54
Iron	4478.00	2963.00
Nickel	108.00	44.53
Zinc	2040.00	1014.00

As can be seen from the results set forth in Table XVII above, cadmium and lead were removed and recovered from the waste stream at efficiencies of greater than 95% and the other metals were removed and recovered at efficiencies ranging from about 18% to about 58%.

**Example 26**



This example illustrates the method of the invention to recover and reclaim metals and other compounds from solid waste materials. In this example, a chemical precipitation process is used to first dissolve them into a liquid matrix and then complex them into a form preferred by end users such as smelters, refineries, and the like. The products recovered from this embodiment of the invention are readily available in their metallic state and are not rendered unusable because they had been previously complexed with hydroxides or sulfides.

The method of the invention illustrated in this example was applied to a hazardous sludge resulting from a pharmaceutical manufacturing process. The sludge had been treated with hydroxides so that the metals were not readily available for reclamation but were, instead, in the form of a toxic sludge that could readily leach into the environment. In this embodiment of the invention, the toxic sludge was first treated with a strong acid such as sulfuric acid or hydrochloric acid to dissolve the hazardous waste materials and form a liquid matrix. The pH of the liquid matrix was then adjusted to form about 5 to about 9 with a suitable base such as sodium hydroxide. A complexing agent such as sodium dimethyldithiocarbamate or zinc dimethyldithiocarbamate was then added to the liquid matrix to form a sludge precipitate from which the metals were recovered and reclaimed thereby completely abating the hazard contained in the toxic sludge. The results obtained are set forth in Table XVIII below.

TABLE XVIII

ELEMENT	SLUDGE	PRODUCT
	(mg/kg)	Pounds reclaimed/Dry Ton
Arsenic	44.56	0.54
Aluminum	7,622.00	92.33
Barium	144.90	1.79
Beryllium	8.63	0.10
Cadmium	74.03	0.90
Chromium	27.98	0.34
Copper	218.80	2.65
Iron	21,360.00	258.74
Lead	334.70	4.05
Manganese	369.80	4.48
Nickel	40.64	0.49
Selenium	42.45	0.51
Zinc	119,000.00	1,441.46

It will be appreciated that the relatively high recovery of zinc resulting from this embodiment will generate increased revenues.

#### Example 27

This example illustrates the method of the invention wherein a metallic complexing agent is used to selectively separate and remove targeted metals at different stages. The complexing agent that can be used in this embodiment can be zinc or sodium dimethyldithiocarbamate or a salt thereof or mixtures thereof that enables a metallic precipitate to form at each stage of the treatment that is more valuable than the precipitate that would have formed if all metals were separated and removed in a single step at a common pH.

In this embodiment, the method of the invention was used to treat an acid mine waste effluent in two stages according to the following sequence:

(1) waste effluent was delivered to a process tank and the pH was adjusted to between about 4 and 6;

<http://patft.uspto.gov/netacgi/nph-Parser?Sect1=PTO1&Sect2=HITOFF&d=PALL&p=1&u=/n...> 3/3/02

- (2) a complexing agent was then Introduced into the tank;
- (3) a metallic precipitate formed that was transported to a filter press for recovery of a Stage 1 product;
- (4) the Stage 1 effluent was routed to a secondary process tank, pH of the effluent was adjusted to from between about 8 and 10, and a complexing agent was introduced into the tank;
- (5) the second metallic precipitate that formed was transported to a filter press to recover a Stage 2 product; and,
- (6) the Stage 2 effluent was discharged.

The results obtained are set forth in Table XIX below which is shown in two sections; one for Stage 1 recovered product and one for Stage 2 recovered product.

TABLE XIX  
STAGE 1

ELEMENT	INFLUENT (ppm)	STAGE 1 EFFLUENT (ppm)	STAGE 1 RECOVERY (%)
Arsenic	0.032	<0.005	84.38
Aluminum	13,310.00	101.770	92.23
Barium	0.911	<0.001	99.89
Cadmium	0.425	<0.002	99.33
Chromium	<0.005	<0.005	00.00
Cobalt	2.139	<0.003	99.86
Copper	23,204.000	<0.002	100.00
Iron	11.982	<0.005	99.96
Lead	0.091	<0.025	72.53
Magnesium	396.500	317.540	19.91
Manganese	176.100	0.250	99.86
Nickel	23.381	<0.010	99.96
Silver	0.133	<0.003	97.74
Zinc	19,649.000	16,788.000	14.56

TABLE XIX  
STAGE 1

ELEMENT	INFLUENT (ppm)	STAGE 1 EFFLUENT (ppm)	STAGE 1 RECOVERY (%)
Arsenic	0.032	<0.005	84.38
Aluminum	13,310.00	101.770	92.23
Barium	0.911	<0.001	99.89
Cadmium	0.425	<0.002	99.33
Chromium	<0.005	<0.005	00.00
Cobalt	2.139	<0.003	99.86
Copper	23,204.000	<0.002	100.00
Iron	11.982	<0.005	99.96
Lead	0.091	<0.025	72.53
Magnesium	396.500	317.540	19.91
Manganese	176.100	0.250	99.86
Nickel	23.381	<0.010	99.96
Silver	0.133	<0.003	97.74
Zinc	19,649.000	16,788.000	14.56

Although, the present invention has been described in considerable detail and with reference to certain preferred embodiments thereof, other variations are possible. Therefore, the spirit and scope of the appended claims should not be limited to the description of the preferred embodiments contained herein.

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<u>3143492</u>	Aug., 1964	Bullock	209/127.
<u>4119533</u>	Oct., 1978	Saitoh et al.	209/173.
<u>4199109</u>	Apr., 1980	Watanabe.	
<u>4529506</u>	Jul., 1985	Smit	209/173.
<u>4557827</u>	Dec., 1985	Fricke et al.	209/127.
<u>4617111</u>	Oct., 1986	Grimm et al.	209/173.
<u>4728045</u>	Mar., 1988	Tomaszek.	
<u>4797201</u>	Jan., 1989	Kuppers et al.	209/127.
<u>4830188</u>	May., 1989	Hannigan et al.	209/173.
<u>4849116</u>	Jul., 1989	Weinmann et al.	209/173.
<u>4944868</u>	Jul., 1990	Jay, Sr. et al.	209/173.
<u>5115987</u>	May., 1992	Mithal	209/173.
<u>5255859</u>	Oct., 1993	Peacock et al.	209/173.

#### Foreign Patent Documents

279200	Aug., 1988	EP.
940341	Feb., 1956	DE.
2101585	Feb., 1973	DE.
136956	Aug., 1979	DE.
3618058	Feb., 1987	DE.
2078138	Jan., 1992	GB.

#### Other References

Patent Abstracts of Japan, vol. 8, No. 138 (C-231) (1575), 27 Jun. 1984.

*Primary Examiner:* Dayoan; D. Glenn  
*Attorney, Agent or Firm:* Collard & Roe

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#### Claims

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We claim:

1. Process for the separation of crushed plastic particles of a plastic mixture of plastics of a chemically different type, which partly have an overlapping density range and partly a different density range selected from the group consisting of polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC), comprising the steps of

first separating the plastic particles having a different density range according to the principle of density separation; and

second separating the plastic particles with the same density range via a free-fall separator;

subjecting the plastic mixture to a surface treatment; and

<http://patft.uspto.gov/netacgi/nph-Parser?Sect1=PTO1&Sect2=HITOFF&d=PALL&p=1&u=/n...> 3/3/02

triboelectric charging the plastic mixture.

2. Process according to claim 1, further comprising the step of providing a separation liquid;

wherein the density of the separation liquid is selected in such a way that the density is between the greatest density and the least density of the individual plastics.

3. Process according to claim 1, further comprising the steps of

washing the separation liquid out of the plastic mixture by water after the first step of density separation.

4. Process according to claim 3, further comprising the steps of

reducing the plastic mixture by a dehydration aggregate, to a residual water proportion of under 2%; and

drying the plastic mixture after the washing.

5. Process according to claim 4 further comprising the steps of

subjecting the dried plastic mixture to a thermal treatment at 70.degree. to 100.degree. C. over a time period of at least 5 minutes.

6. Process according to claim 2, further comprising adjusting the density of the separation liquid to values between 1.0 and 1.3 g/cm.<sup>3</sup>.

7. Process according to claim 1, comprising triboelectric charging of the plastic mixture at a temperature of 15.degree. to 50.degree. C., and at a relative humidity of the ambient air of 10 to 40.

8. Process according to claim 1, comprising triboelectric charging the plastic mixture by loading in a fluidized-bed dryer.

9. Process according to claim 1, further comprising passing the plastic mixture through a spiral worm of sufficient length.

10. Process according to claim 1, further comprising conveying the plastic mixture pneumatically over a specified distance.

11. Process according to claim 1, further comprising operating the free-fall separator at a field intensity of 2 to 3 KV/cm.

12. Process according to claim 7, wherein the triboelectric charging of the plastic mixture occurs at a temperature of 20.degree. C. to 35.degree. C. and at a relative humidity of the ambient air of 15% to 20%.

13. Process for the separation of plastic particles of a plastic mixture of plastics of a chemically different type, which partly have an overlapping density range and partly a different density range, selected from the group consisting of polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC), comprising

in a first step, the plastic particles having a different density range are separated from one another according to the principle of density Separation and;

in a second step, the plastic particles with the same density range are separated,

wherein the density of a separation liquid is selected in such a way that the density is between the greatest density and the least density of the individual plastics, and

wherein the separation liquid is selected in such a way that it is either in the basic range having pH about 11 to 12 or in the acid range having pH about 2 to 4.

14. Process according to claim 13, wherein the separation liquid is a salt solution of which the main component is NaCl.

15. Process according to claim 14, wherein K-, Mg- and SO.sub.4 -ions are additionally present.

16. Process for the separation of plastic particles of a plastic mixture of plastics of a chemically different type, which partly have an overlapping density range and partly a different density range, selected from the group consisting of polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC), comprising

in a first step, the plastic particles having a different density range are separated from one another according to the principle of density separation;

in a second step, the plastic particles with the same density range are separated;

washing the separation liquid out of the plastic mixture by water after the first step of density separation;

reducing the plastic mixture by a dehydration aggregate to a residual water proportion of under 2% prior to drying;

drying the plastic mixture after washing; and

adding an organic substance to the plastic mixture.

17. Process according to claim 16, wherein the organic substance is a fatty acid.

18. Process according to claim 17, further comprising adding the fatty acid in an amount of 10 to 50 mg/kg plastic mixture.

19. Process according to claim 16, wherein the plastic particles of the plastic mixture have a size of under 10 mm.

20. Process according to claim 19, wherein the plastic particles of the plastic mixture have a size under 6 mm.

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*Description*

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marginal conditions it is necessary to maintain in the triboelectric charging temperatures of about 15.degree. to 50.degree. C., preferably 20.degree. to 35.degree. C., and a relative humidity of the ambient air of 10 to 40%, preferably 15 to 20%. The triboelectric charging of the plastic particles themselves takes place in the known way by intimately contacting of the particles with one another.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a flow diagram relating to Example 1;

FIG. 2 shows a flow diagram relating to Example 2; and

FIG. 3 shows a flow diagram relating to Example 3.

The process according to the invention is explained on the basis of the following examples.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

### EXAMPLE 1:

Separation of a mixture of beverage bottles is shown in FIG. 1

The mixture of beverage bottles used had the following composition:

76.9% PET

19.8% PVC

2.1% PE

1.2% paper/dirt.

The bottle mixture was fed into a wet-operating cutting mill and, under addition of water, crushed to a particle size of under 6 mm. The dirt solution, which also contained paper, was drawn off. Subsequently, the material was vigorously stirred in a washer, which cleaned the surfaces and prepared the latter for the later electrostatic separation.

For separating the polyolefins (PE), the substances was admitted into a hydrocyclone. The resulting PVC-PET--mixture was separated from the liquid on a vibration screen, centrifuged, and dried for 6 minutes in a fluidized-bed dryer at 70.degree. to 100.degree. C.

In the fluidized bed, any last paper residues that might still be present can be discharged with the exhaust air and separated from the exhaust air by means of a cyclone. The predried material was subsequently contacted in another fluidized-bed dryer for another 3 minutes at 30.degree. C. and at the same time charged.

The material draining from the fluidized bed was continuously admitted to a separating plant consisting of two separators. A PET-concentrate with 99.4% PET is obtained already in the preliminary separation; the PVC-concentrate with a PVC-content of 82.3% was conveyed to the after-separation separator by means of a spiral worm, whereby the selective charging of the plastic particles developed.

In the after-separation separator, the preconcentrate so charged was separated into a high-percent PVC-

concentrate, a medium-material fraction, and a deconcentration fraction containing about 53% PET. The latter together with the medium material of the preseparation was recycled into the fluidized bed for new charging.

All in all, it was possible to separate the plastic mixture into

a PVC-fraction with a degree of purity of 99.3% PVC,

a PET-fraction with a degree of purity of 99.4% PET, and

a PE-fraction with a degree of purity of 97.6 PE;

the yield (absolute quantity)--based on the bottle mixture used--consisted of:

94.6% PET

96.2% PVC

89.7% PE.

#### EXAMPLE 2:

Separation of a PE/PP/PS/PVC plastic mixture is shown in FIG. 2

The used mixture of used plastic articles contained four of the most commonly used mass plastics in the following composition:

45.7% PE

20.1% PP

17.5% PVC

14.9% PS

1.8% residual substances.

100 kg of said mixture was first completely crushed on a cutting mill to a grain size of under 6 mm. The shred mixture was fed into a washer and stirred with fresh water. The washed material was transferred into a flotation basin filled with water, whereas the dirt solution was discarded. The light fraction containing the polyolefins was skimmed off, whereas the heavy fraction containing the PVC and PS was sucked off at the bottom of the basin. Both fractions were predehydrated by means of centrifuging.

The PP/PE-fraction was fed into a fluidized-bed dryer and dried for 6 minutes at 80.degree. C. A fatty acid mixture C8-C12 was sprayed onto the draining material in an amount of 50 g/t, and fluidizing was carried out in another fluidized-bed dryer for 3 minutes at 30.degree. C. The mixture flowing from the fluidized bed was continuously fed into a free-fall separator. The medium material of said separation was continuously recycled into the second fluidized-bed dryer.

The electrostatic separation of the light fraction supplied the following result:



concentrate, a medium-material fraction, and a deconcentration fraction containing about 53% PET. The latter together with the medium material of the preseparation was recycled into the fluidized bed for new charging.

All in all, it was possible to separate the plastic mixture into

a PVC-fraction with a degree of purity of 99.3% PVC,

a PET-fraction with a degree of purity of 99.4% PET, and

a PE-fraction with a degree of purity of 97.6 PE;

the yield (absolute quantity)--based on the bottle mixture used--consisted of:

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96.2% PVC

89.7% PE.

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Separation of a PE/PP/PS/PVC plastic mixture is shown in FIG. 2

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17.5% PVC

14.9% PS

1.8% residual substances.

100 kg of said mixture was first completely crushed on a cutting mill to a grain size of under 6 mm. The shred mixture was fed into a washer and stirred with fresh water. The washed material was transferred into a flotation basin filled with water, whereas the dirt solution was discarded. The light fraction containing the polyolefins was skimmed off, whereas the heavy fraction containing the PVC and PS was sucked off at the bottom of the basin. Both fractions were predehydrated by means of centrifuging.

The PP/PE-fraction was fed into a fluidized-bed dryer and dried for 6 minutes at 80.degree. C. A fatty acid mixture C8-C12 was sprayed onto the draining material in an amount of 50 g/t, and fluidizing was carried out in another fluidized-bed dryer for 3 minutes at 30.degree. C. The mixture flowing from the fluidized bed was continuously fed into a free-fall separator. The medium material of said separation was continuously recycled into the second fluidized-bed dryer.

The electrostatic separation of the light fraction supplied the following result:

Quantity kg	Analysis	Yield
	(degree of purity in %)	(in % of the charge)
PE-fraction		
44.1	96.6	92.2
PP-fraction		
20.6	88.5	90.7

The heavy fraction was transferred into a fluidized-bed dryer with a connected cooler, dried in the heating zone for about 6 minutes at 80.degree. C., and fluidized in the cooling zone for about 3 minutes at 30.degree. C. The electrostatic separation, with recycling of the medium material in this case too, supplied the following result:

Quantity kg	Analysis	Yield
	(degree of purity in %)	(in % of the charge)
PVC-fraction		
17.3	97.1	95.9
PS-fraction		
14.8	94.3	93.7

### EXAMPLE 3:

Separation of a PE/PS/PET/PVC-mixture into the individual components is shown in FIG. 3

The used mixture of used plastics had the following composition:

46.8% PE

29.8% PS

12.2% PVC

10.1% PET

1.1% dirt.

100 kg of said mixture was first completely crushed in a cutting mill to a grain size of under 6 mm. The shred mixture was fed into a washer and stirred with fresh water. The washed material was filled in a flotation basin filled with potash waste liquor with a density of 1.2 g/cm.<sup>sup.3</sup>.

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( 1 of 1 )

**United States Patent****5,290,401****Savisalo , et al.****March 1, 1994**

### Method and a device for separating plastic particles from suspensions

#### Abstract

The invention relates to a method for separating plastic particles (P) from a suspension (L), e.g. from a cellulose mass or cellulose pulp suspension, in which the fiber-floc material is broken for loosening the plastic particles (P). In the method, turbulent flows are caused to said suspension (L), by means of which flows the particles (P) to be separated are separated from the remaining mass as the fiber network is decomposing, whereby lighter particles (P) are separated. In the method, the suspension (L) obtained in the previous phase is subjected to such a treatment that a concentration difference is achieved, which prevents the fiber network from reforming and thereby the plastic particles (P) from binding thereto, and a flow (F) is directed to the separation point, where the plastic particles (P) are separated from the suspension (L). The invention also relates to a device for separating plastic particles from suspensions, especially cellulose and paper fiber suspensions, which device comprises a container (12) and guiding means (13,14) fitted thereto for achieving turbulent flows and means (23,24,25) for diluting and/or orientating the suspension and which device further comprises separating means (19) for separating the particles from the suspension.

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209/155; 209/156**Intern'l Class:**

D21B 001/32

**Field of Search:**162/4,55 204/130,132,140 209/12,155,156,173,127.1,129.0,2  
241/14,20,40,41

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**References Cited [Referenced By]**

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**U.S. Patent Documents**

<u>914368</u>	Mar., 1909	Boudot	204/132.
<u>1008779</u>	Nov., 1911	Bonser	204/132.
<u>2743178</u>	Apr., 1956	Kronel	162/4.
<u>2916216</u>	Dec., 1959	Altmann	162/4.
<u>3025213</u>	Mar., 1962	Copeland	162/4.
<u>3098784</u>	Jul., 1963	Gorman	162/5.
<u>3173827</u>	Mar., 1965	Altmann et al.	162/4.
<u>3284282</u>	Nov., 1966	Immel	162/55.
<u>3615014</u>	Oct., 1971	Hruby	162/4.
<u>3835006</u>	Sep., 1974	Fujita et al.	204/180.
<u>4000031</u>	Dec., 1976	Açobas	162/4.
<u>4219381</u>	Aug., 1980	Schnell	162/4.
<u>4483768</u>	Nov., 1984	Gazzoni	209/173.
<u>4650570</u>	Mar., 1987	Fjallstrom	162/55.
<u>5062932</u>	Nov., 1991	Pulliainen	204/130.
<u>5110454</u>	May., 1992	Parker et al.	209/173.

**Foreign Patent Documents**

7803035	May., 1979	FI.
822894	Feb., 1983	FI.
81393	May., 1990	FI.
9014890	Dec., 1990	WO.
8125510	Oct., 1982	GB.

*Primary Examiner:* Jones; W. Gary*Assistant Examiner:* Lamb; Brenda*Attorney, Agent or Firm:* Steinberg & Raskin

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**Claims**

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**We claim:**

1. A method for separating plastic particles from a cellulosic pulp suspension, comprising

flowing a suspension into a container containing plastic particles within a decomposable fiber network whereby turbulent flows are produced such that the particles are separated from the suspension as the fiber network decomposes,

manipulating the flow of the suspension after the particles have been separated therefrom such that the fiber network is prevented from reforming and thereby the separated plastic particles are prevented from binding thereto, and

directing the suspension and separated plastic particles to a removal point, where the plastic particles are mechanically and electrically separated and removed from the suspension.

2. A method according to claim 1, further comprising guiding the plastic particles to a surface of the container and flowing the plastic particles into an overflow of the container.

3. A method according to claim 1, wherein the plastic particles are separated at the removal point by collecting the plastic particles by means of collecting scoops of a collector.

4. A method according to claim 1, wherein said plastic particles are electrically separated and removed from the suspension to an electrode having a suitable potential in a DC source-electrode system connected to the container.

5. A method according to claim 1, further comprising treating the suspension containing plastic particles at the removal point by diluting the suspension such that a consistency gradient is intensified and a loss of fiber from the suspension is eliminated.

6. A method according to claim 1, further comprising providing guide means to produce the turbulent flows.

7. A method according to claim 6, wherein the guide means comprise guide plates.

8. A method according to claim 1, wherein the flow of the suspension is manipulated by means of liquid jets.

9. A method as claimed in claim 1, further comprising flowing the suspension into the container such that as a result of turbulent flows in the container, the plastic particles rise to an upper surface of the container based on a weight difference between the plastic particles and the fiber network of the suspension.

10. A method as claimed in claim 9, wherein the removal point is located at an end of the container opposite a point at which the suspension enters the container such that the suspension flows through the container.

11. A method as claimed in claim 1, wherein the flow of the suspension is manipulated by means of a liquid jet arranged within said container such that the separated plastic particles travel in an area of turbulence produced by the liquid jet between the separation point and the removal point thereby preventing the plastic particles from binding to the decomposed fiber network.

12. A device for separating plastic particles from cellulosic fiber suspensions containing plastic particles in a fiber network comprising

a container having an intake for a cellulosic fiber suspension,

guiding means arranged within said container for producing turbulent flows in said container such that plastic particles in the suspension separate from a fiber network of the suspension,

manipulating means for manipulating the flow of the suspension in said container such that the separated plastic particles are prevented from binding to the fiber network, said manipulating means being arranged within said container, and

removal means for mechanically and electrically removing the plastic particles from the suspension, said removal means being located above said guiding means and said manipulating means and arranged in said container.

13. A device according to claim 12, wherein said guiding means comprise guide plates.

14. A device according to claim 12, wherein said manipulating means comprise a plurality of liquid jets.

15. A device according to claim 12, wherein said removal means comprise a wire collector and collecting scoops attached to said wire collector.

16. A device according to claim 12, wherein said removal means comprise an overflow opening arranged at an edge of said container.

17. A device according to claim 12, wherein said removal means comprise a DC source-electrode system, said system comprising an electrode whose potential is arranged in such a way that the plastic particles are guided thereto.

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### *Description*

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The invention relates to a method for separating plastic particles from a suspension, e.g. from a cellulose mass or cellulose pulp suspension, in which the fiber-floc material is broken for loosening the plastic particles.

The invention also relates to a device for separating plastic particles from a suspension, e.g. from a cellulose mass and paper fiber suspension.

In many previously known solutions, the removal of the plastic from among the cellulose fibers has mainly been based on the density of the plastic, either in a liquid phase or in centrifugal methods.

The earlier FI patent application 885180 or U.S. Pat. No. 5,062,932 by the applicant describes a method and a device for separating plastic particles from solutions, which approach is based on an electrical separation of plastic particles. In this known method, the plastic particles in the solution have been separated electrically by placing in the solution an anode and a cathode and by adjusting the potential of the anode and the cathode so that it is possible to separate the plastics from the solution.

The object of the present invention is to provide a method and a device for separating plastics from a suspension, e.g. cellulose suspension, to be able to analyze the quantity of the plastics in the suspension

and perform necessary studies, related e.g. to the origin and quality of the plastic, etc.

The method according to the invention is mainly characterized in that in the method

- a) turbulent flows are caused to said suspension, by means of which flows the particles to be separated are separated from the remaining mass as the fiber network is decomposing, whereby lighter particles are separated,
- b) the suspension obtained in the phase a) is subjected to such a treatment that a concentration difference is achieved, which prevents the fiber network from reforming and thereby the plastic particles from binding thereto, and
- c) a flow is directed to the separation point, where the plastic particles are separated from the suspension.

The device according to the invention is mainly characterized in that the device comprises a container and guiding means fitted thereto for achieving turbulent flows and means for diluting and/or orientating the suspension and that the device further comprises separating means for separating the particles from the suspension.

In other embodiments of the present invention, the plastic particles are separated from the suspension at a separation point either mechanically, electrically, or both. The plastic particles (P) can also be separated by means of a collecting scoops on a collector or guided to a surface of the container and then separated into an overflow of the container. Other possible embodiments are described.

It is essential in the inventive method and device that the turbulence causes the breaking of the fiber/floc material as a result of shearing forces. The turbulence can be achieved by means of a liquid jet, as described above, but it is also possible to use a rotatable cylindrical rotor, or by allowing two separate mass flows to collide against each other. In addition, the turbulence can also be achieved so that a mass suspension is sprayed within the mass suspension by means of pressure. It is also possible to mix the mass mechanically under the surface.

It is also essential in the inventive method and device that the height of the turbulence area is low, whereby the plastic particles have a short way to transfer to the surface of the suspension material container. It is also advantageous that another turbulence area is achieved after the first guide plate. Different consistency gradients are caused to the suspension in the container by the interaction of the turbulences and the liquid flows. The plastic particles can then loosen from the fiber/floc material and cannot return to the fiber. For intensifying the consistency gradients, it is also possible to add to the surface of the suspension material mixture a material with a consistency of 0% by spraying thereon e.g. more liquid.

Instead of the flow guiding plates, the flow can also be guided e.g. by changing the shapes of the container.

It is also possible to break the fiber/floc material for loosening the plastic particles so that a momentary reduction is caused to the suspension flow.

In the inventive method and device, the separation of the plastic is based on the breaking of the fiber material binding the plastic particles by means of a turbulence and pressure jets, whereby the particles are released and rise to the surface as a result of a consistency gradient thus formed. The plastics can be collected from the surface either electrically and/or mechanically.

When separating plastic from e.g. cellulose, the inventive device is preferably located in a sorting space e.g. after the second or third sorting, resulting from the enrichment of the plastics in the flow-off.

The inventive method and device are next described in detail with reference to the figures of the accompanying drawing, to which the invention is not intended to be narrowly limited in any way.

FIG. 1 shows schematically the inventive device for realizing the inventive method, in which device the plastic particles which have risen to the surface are removed to an overflow.

FIG. 2 shows schematically the inventive device for realizing the inventive method, in which device the plastic particles which have risen to the surface are removed mechanically by means of a collector.

FIG. 3 shows schematically the inventive device for realizing the inventive method, in which device the plastic particles which have risen to the surface are removed electrically by means of a collector.

FIG. 4 shows schematically the inventive device for realizing the inventive method, in which device the plastic particles which have risen to the surface are removed both mechanically by means of a collector and to an overflow.

The principle of the invention is based on the fact that the plastics, which are intended to be separated from the suspension, are lighter than the fiber material in the suspension, whereby the plastics inherently tend to rise to the surface of the suspension. The rising of the plastics to the surface is in most conditions, e.g. in laminar flow conditions, when the solids content is more than 0.02% by weight, is prevented by the fiber and floc material. In order to be able to release the plastics, the fiber/floc material, or the floccule, has to be decomposed. When the flocs have been decomposed, the plastics rise to the surface, from which they can be collected.

According to FIG. 1, a suspension L is led into a container 12 via a feeding pipe 15 and a feeding valve 16. When the suspension L has entered the container 12, its flow F is guided with a guide plate 13 so that the direction of the fiber flow F is towards a surface layer S of the container 12. In FIG. 1, the plastic particles are designated with a reference letter P. The suspension L is then led with a liquid jet 23 along the liquid surface S of the container 12 and further by means of a second liquid jet 24, a guide plate 14 and a third liquid jet 25 towards an overflow opening 19 of the container 12. The liquid jets 23,24,25 to be directed to the flow F cause a shearing stress and turbulence to the floc material, whereby the plastic particles P are released from the floc material and rise to the surface S of the container 12.

From the overflow opening 19 the flow F.sub.P containing plastic particles P is led into a container 30. A portion F.sub.L of the suspension containing fiber and floc material and released from the plastic particles P is led out of the container via a discharge valve 18 and a discharge pipe 17.

In the embodiment of FIG. 2, a device 102 is comprised of the container 12, into which the suspension L is led via the feeding pipe 15 and the feeding valve 16. The suspension advances as the flow F guided by the guide plate 13, until it arrives at the liquid jet 24, which liquid jet causes the decomposition of the fiber/floc material by the action of a turbulence and shearing stress. The plastic particles P releasing from the fibers and the flocs and the suspension L is led further as the flow F towards the liquid surface S of the container 12.

In the immediate vicinity of the liquid surface S of the container 12 is fitted in the embodiment of FIG. 2 a wire collector 20, which is provided with transverse collecting scoops 21. The wire collector 20 rotates around guide rolls 28, 29 in its rotational direction D. The scoops 21 then collect the plastic particles P



from the surface S of the suspension L. The wire collector 20 conveys the plastic particles P further as the flow F.sub.P into a discharge container 30. A suspension flow F.sub.L containing liquid, flocs and fibers is led via the discharge valve 18 and the discharge pipe 17 out of the container 12.

In the embodiment of FIG. 3, the collection of the plastic particles P in a device 103 is based on an electrical separation. The suspension L is led into the container 12 via the feeding valve 16 and the feeding pipe 15, and the flow is guided with the guide plate 13 and the fiber/floc material is decomposed with the liquid jet 24, and the flow F is guided further with the guide plate 14. The plastic particles P are collected with the wire collector 20 provided with the collecting scoops 21. The plastic particles P are collected on the basis of potential differences, and the electrodes in the suspension are designated with reference numbers 37 and 38. The comparison electrode is marked with a reference number 36. From a power source 35 is also led a current to the wire collector 20, which is then charged electrically, forming its own electrode 40.

The plastic particles P are collected from the suspension L in the container 12 in such a way that a voltage is caused to the electrodes 37,38 and 40 by the action of the power source 35, e.g. a DC source. When a potential difference prevails between the electrodes 37,38 and 40, the particles P attach to an electrode having a suitable potential, most suitably to the wire collector electrode 40. The potential of the remaining electrodes 37,38 and 40 is monitored by means of the comparison electrode 36 and the potential of the electrodes 37,38 and 40 is controlled on the basis of the measurement results of the comparison electrode 36 so that they remain suitable, i.e. such that the plastic particles P are guided to the wire collector acting as the electrode 40.

The plastic particles P are removed as the flow F.sub.P from the wire collector 20 acting as the electrode 40 to the container 30. The remaining portion of the suspension L, i.e. the liquid material and the fiber material as well as the flocs, leaves as the flow F.sub.L via the discharge valve 18 and the discharge pipe 17.

The embodiment of a device 104 shown in FIG. 4 is a combination of the devices 101 and 102 shown in FIG. 1 and 2 in such a way that the removal of the plastic particles P occurs as two flows F.sub.P1 and F.sub.P2 such that the flow F.sub.P1 is removed by means of the wire collector 20 and collecting scoops 21 and the flow F.sub.P2 leaves directly as an overflow for the container 30.

In addition to the open-pool type constructions shown in the figures, the inventive devices for realizing the inventive method can be adapted to operate under pressure.

The inventive devices described above can, for realizing the inventive method, be placed one after the other or side by side so that any embodiment can be combined with any embodiment.

The invention has above been described with reference to its preferable embodiments, but the intention is not to limit the invention in any way to this example, but many changes and modifications are possible within the inventive idea defined in the enclosed patent claims.

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The light fraction containing PE and PS was skimmed off, whereas the heavy fraction containing PVC and PET was sucked off at the bottom of the basin. Both fractions were predehydrated on a swing screen, washed with fresh water, and subsequently predehydrated on centrifuges to an adhering moisture of 2%. The salt-containing waste waters collected in the density separation and predehydration can be recycled into the potash dissolving operation for treatment. Both fractions were fed into separate fluidized-bed dryers equipped in each case with a heating and a cooling zone. In the hot zone, the materials were heated to 80.degree. C., whereby the dwelling time came to about 6 minutes, whereas the cooling zone connected downstream was operated with unheated air.

The materials flowing from the fluidized beds were fed into electrostatic free-fall separators, whereby the collected medium materials were recycled into the fluidized beds.

The electrostatic separation of the light fraction supplied the following result:

Quantity kg	Analysis	Yield
	(degree of purity in %)	(in % of the charge)
PE-fraction		
43.8	95.6	93.5
PS-fraction		
27.7	92.4	92.9

The following result was obtained in the electrostatic separation of the heavy fraction:

Quantity kg	Analysis	Yield
	(degree of purity in %)	(in % of the charge)
PVC-fraction		
12.6	93.9	96.6
PET-fraction		
9.2	97.1	88.0

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This application is a continuation of application Ser. No. 025,010, filed Mar. 29, 1979, now abandoned.

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*Claims*

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What I claim is:

1. A process for reclaiming low density moisture absorbent materials from a material mixture, comprising:

inputting a material mixture containing high and low density moisture inabsorbent and low density moisture absorbent materials

selectively and controllably applying moisturizers to said material mixture and increasing the moisture content of said material mixture to a predetermined value to moisturize said low density absorbent materials and increase the weight and density thereof to form high density moisturized materials and a moisture weighted material mixture;

establishing a centrifugal field and segregating said moisture weighted material mixture in said field to produce a high density fraction and a low density fraction;

partially fiberizing said high density moisturized materials to selectively reduce the size thereof;

separating said segregated high density fraction into an oversize and an undersized fraction; and collecting the undersized fraction as recovered product and discharging the oversized fraction as an unreclaimed product.

2. The process of claim 1 further comprising:

selectively removing the low density fraction from the centrifugal field by creating controlled axial air streams within the centrifugal field.

3. The process of claim 2 wherein said axial controlled air streams are created in said centrifugal field by inducing a low pressure region at the bottom of said centrifugal field thereby creating said axially directed air streams through the center portion of said field to extract lightweight nonrefined discarded materials.

4. The process of claim 3 wherein said lightweight and nonrefined discarded materials are introduced in a cyclone classifier to be cleaned of lightweight plastic materials by feeding said mixture to a moisture control section for selectively and controllably increasing the moisture content of said mixture to a predetermined value for increasing the weight and moisture content of said nonrefined materials for forming a moisture weighted mixture;

feeding said moisture weighted material mixture into a centrifugal field for fiberizing and segregating said weighted and moisturized materials of said moisturized weighted mixture;

subjecting at least part of said centrifugally segregated and fiberized weighted and moisturized materials to an abrasion means for additionally fiberizing said materials;

propelling said abraded centrifugally segregated fiberized, weighted and moisturized materials against a classifier means for discharging therethrough undersized centrifugally segregated and fiberized weighted and moisturized materials.

5. The process of claim 3 wherein said lightweight and nonrefined discarded materials are introduced in a cyclone classifier to be cleaned of lightweight plastic materials by selectively and controllably applying moisturizers to said materials for increasing the moisture content of said materials to a predetermined value to increase the weight and moisture of said nonrefined materials to form a moisture weighted material mixture;

subjecting said moisture weighted material mixture to reduction forces to fiberize and refine said moisturized materials to a predetermined size;

separating refined and fiberized moisturized materials from said mixture as a recovered product.

6. The process of claim 1 wherein said segregating of said moisture weighted material mixture is accomplished by centrifugally suspending said low density moisture absorbent material in a central portion of said field and displacing said high density inabsorbent and high density moisturized materials in a peripheral portion of said field.

7. The process of claim 1 further comprising separating said unreclaimed oversized fraction into a high density fraction and into a low density fraction; controlling the water content of the high density fraction; to a predetermined level and mixing the water controlled high density fraction with said moisture weighted material mixture in said centrifugal field.

8. The process of claim 7 wherein the moisture content of said material mixture is controlled to between 20 and 35 percent.

9. The process of claim 7 wherein the moisture content of said moisture weighted material mixture is controlled at 25 percent.

10. A process for the recovery of cellulose fibers from LW-MSW comprising:

(a) cutting the LW-MSW to a size between 2" and 6" ;

(b) segregating the LW-MSW in a centrifugal field into a high density fraction and a low density fraction;

(c) removing the heavy undersized contaminants including grit, glass and vegetable matter from the cut, segregated LW-MSW;

(d) controlling the moisture content of the decontaminated LW-MSW to a predetermined level;

(e) partially fiberizing the paper fraction of the moisture controlled LW-MSW to selectively reduce the size of the paper;

(f) segregating the LW-MSW in a centrifugal field into a high density fraction and a low density

fraction;

(g) separating said centrifugally segregated high density fraction into an oversized and undersized fraction; and collecting the undersized fraction as recovered product;

(h) selectively removing the low density fraction from said centrifugal field by inducing a controlled air stream within said centrifugal field.

11. The process of claim 10 wherein the controlled air streams are formed by inducing a low pressure region at the bottom of the centrifugal field thereby creating a downward air flow through a central portion of said centrifugal field.

12. The process of claim 11 wherein the moisture content is controlled to a level between 20 and 35 percent.

13. The process of claim 12 wherein the moisture content is controlled to a level of approximately 25 percent.

14. The process of claim 10 wherein in step g the undersized fraction is separated from the oversized fraction by screening.

15. An apparatus for separating cellulose fiber from a chopped paper-plastic mixture comprising:

(a) means to control the moisture content of the paper-plastic mixture;

(b) means to partially fiberize the paper fraction of the moisture controlled paper plastic mixture;

(c) means to induce a centrifugal field to separate the paper-plastic mixture into a high density region and a low density region;

(d) screen means surrounding the centrifugal field means adapted to segregate the undersized fraction of the high density fraction from the oversized fraction;

(e) means to collect the segregated undersized fraction.

16. The apparatus of claim 15 further comprising:

(f) means to create directed air streams in the centrifugal field to selectively remove the low density fraction.

17. An apparatus for separating cellulose fiber from a chopped paper-plastic mixture comprising:

(a) means to control the moisture content of the paper-plastic mixture;

(b) a rotor chamber in communication with said moisture control means to partially fiberize the paper component of the paper-plastic mixture and to induce a centrifugal field to separate the paper-plastic mixture into a high density fraction and a low density fraction;

(c) a classifier screen surrounding the rotor chamber and adapted for the passage of the partially fiberized paper fraction of the paper mixture;

(d) means to collect the partially fiberized paper passing through the classifier screen;

(e) a blower at the bottom of said rotor chamber to create a low pressure area within said centrifugal field to induce a downward force on the low density fraction in the rotor chamber;

(f) venturi means in communication with said blower to intensify the downward force induced by the blower;

(g) means to collect the paper-plastic mixture from the bottom of the rotor chamber.

18. The apparatus of claim 17 wherein the classifier screen has between 3/4 and 1/4 inch diameter holes.

19. The apparatus of claim 17 further comprising means to direct air from the interior of the rotor chamber in the direction of the classifier screen.

20. A process for treating and separating a mixture of municipal solid waste comprising:

feeding said mixture to a first reduction means for chopping and screening substantially all the heavy materials and metals from the mixture to leave a residual mixture comprising high and low density inabsorbent materials and low density absorbent materials;

feeding said residual mixture to a first rotor chamber and subjecting said mixture to ballistic attrition for removing residual gross contaminants;

feeding said decontaminated residual mixture to a moisture control section for selectively and controllably increasing the moisture content of said decontaminated residual mixture to a predetermined value for increasing the weight and moisture content of said low density absorbent materials for forming a moisturized weighted mixture;

feeding said moisturized weighted mixture into a second centrifugal field for fiberizing and segregating said weighted and moisturized absorbent materials of said moisturized weighted mixture;

subjecting at least part of said centrifugally segregated and fiberized weighted and moisturized absorbent materials to an abrasion means for additionally fiberizing said materials;

propelling said abraded centrifugally segregated and fiberized weighted and moisturized absorbent materials against a classifier means for discharging therethrough undersized centrifugally segregated and fiberized weighted and moisturized materials.

21. The process of claim 20 further comprising inducing a low pressure area below said centrifugal field to induce downward forces on the low density fraction for extracting lightweight and nonrefined material as a discarded material.

22. The process of claim 21 wherein said lightweight and nonrefined discarded materials are introduced in a cyclone classifier to be cleaned to lightweight plastic materials by feeding said mixture to a moisture control section for selectively and controllably increasing the moisture content of said mixture to a predetermined value for increasing the weight and moisture content of said nonrefined materials for forming a moisture weighted mixture;

feeding said moisture weighted mixture into a centrifugal field for fiberizing and segregating said

weighted and moisturized materials of said moisturized weighted mixture;

subjecting at least part of said centrifugally segregated and fiberized weighted and moisturized materials to an abrasion means for additionally fiberizing said materials;

propelling said abraded centrifugally segregated and fiberized weighted and moisturized materials against a classifier means for discharging therethrough undersized centrifugally segregated and fiberized weighted and moisturized materials.

23. The process of claim 21 wherein said lightweight and nonrefined discarded materials are introduced in a cyclone classifier to be cleaned of lightweight plastic materials by selectively and controllably applying moisturizers to said materials for increasing the moisture content of said materials to a predetermined value to increase the weight and moisture of said nonrefined materials to form a moisture weighted material mixture;

subjecting said moisture weighted material mixture to reduction forces to fiberize and refine said moisturized materials to a predetermined size;

separating refined and fiberized moisturized materials from said mixture as a recovered product.

24. An apparatus for reclaiming fibrous materials from a mixture of materials containing high and low density inabsorbent materials and low density absorbent materials comprising:

means for receiving said mixture for selectively and controllably increasing the moisture content of said mixture to a predetermined value by moisturizing said mixture and increasing the weight of said low density moisture absorbent materials for forming a moisture weighted mixture containing high density moisture absorbent materials;

means for inducing a centrifugal field in said moisture weighted material mixture for at least partially fiberizing said high density moisture absorbent materials and segregating said material into high and low density fractions;

means for selectively passing an undersized portion of said high density moisture absorbent materials to output.

25. The apparatus of claim 24 further comprising density separation means to separate the paper-plastic mixture from the bottom of the rotor chamber into a high density and a low density fraction; means to recycle said high density fraction to the moisture control means.

26. The apparatus of claim 25 wherein the density separation means is a cyclone classifier.

27. The apparatus of claim 26 comprising heavy contaminant removal means to remove small high density contaminants such as grit, glass and vegetable matter from the paper-plastic moisture before moisture control means.

28. The apparatus of claim 27 wherein heavy contaminant removal means comprises a rotor chamber; a heavy contaminant classifier screen adapted for the passage of small heavy contaminants.

29. The apparatus of claim 28 wherein the heavy contaminant claims has holes between 1/8 and 1/2 in diameter holes.

30. The apparatus of claim 24 further comprising a means for abrading said high density materials segregated in said centrifugal field.

31. The apparatus of claim 24 wherein said means for selectively passing at least a portion of said moisturized and fiberized weighted absorbent materials to output comprises a screen at least partially surrounding said rotor chamber.

32. The apparatus of claim 24 further comprising means for establishing a low pressure area for creating axial air streams within a central portion of said field and extracting low density materials suspended in said centrifugal field.

33. The apparatus of claim 32 wherein said low pressure flow is created by a venturi means in communication with said chamber.

34. The apparatus of claim 24 wherein said means for inducing a centrifugal field comprises a rotor chamber having spinning shaft and series of rotor blades radially disposed therefrom.

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### *Description*

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## BACKGROUND OF THE INVENTION

### 1. Field of the Invention

This invention relates to the classification of paper from a variety of contaminated paper-plastic mixtures from miscellaneous sources. More specifically for example, this invention relates to the recovery of high grade paper fibers from municipal solid waste (hereinafter MSW) which includes municipal household garbage and trash and includes such trash as is normally collected by a municipality, as for example, household garbage and trash, household yard trash, commercial trash from retail establishments, apartments, offices and warehouses. In addition, this invention relates to a classification method to recover valuable materials from selected wastes such as vegetable fibers, paperboards, agricultural and industrial cellulose materials as well as old corrugated boxes from supermarkets, wadding and molded pulps.

This invention finds particular utility for classification of valuable fibers from the "light weight fraction" of MSW herein after LW-MSW which is composed of mainly papers, textiles, and plastics. The light weight fraction of the MSW is defined as trash MSW which has been first prepared to remove heavy materials such as stones, iron or other metal objects, glass, carpeting, construction debris, wire, rubber, tires, and white goods.

Such materials are removed by solid waste crushing and shredding followed by use of rotary or flat screens, magnets, or otherwise. The present invention enables the recovery of the paper fibers from contaminated paper-plastic mixtures such that the paper cellulose fibers are refined and suitable for direct repulping by paper mills into commercial grade papers, including paper products, molded fibers, building materials, and the like. In addition this product is a suitable fuel. This process also produces other classified products which are suitable fuels and have other uses.

### 2. Description of the Prior Art

Various attempts have been made to find uses for the light weight fraction of MSW. Air classifiers of



various types have been employed which have attempted to recover useable cellulose fibers. Such process provides a cellulose product having limited use since it is contaminated in significant amounts with plastics and other contaminants which can be used only for low grade products such as soil conditioners or fuel.

Other prior art processes have attempted to directly repulp in water the MSW or plastic-paper mixture recovered from MSW. Such process have proved ineffective because of the extreme difficulty in separating the plastics and contaminants from the paper fraction. An example of such a prior art process, which recovered low grade plastic contaminated paper confetti from a paper-plastic mixture, is found in my application Ser. No. 427,301 filed Jan. 7, 1974. Therein combined air classifications were used following steady cooking of the mix followed by drying by forced hot air to attempt reaching a cleaned paper fiber product.

## SUMMARY OF THE INVENTION

It is an object of the present invention to provide a process for recovering cellulose fibers directly from the light weight fraction of MSW which overcomes the disadvantages of known apparatus for paper recovery from MSW.

It is a further object of the present invention to provide an improved process for separating and classifying the components of a paper-plastic mixture.

It is a further object of the present invention to provide a process for recovering cellulose fibers from MSW without adding of heat or steam cooking or heavy uncontrolled wetting.

Another object of the present invention is to provide a process for recovering cellulose fibers from MSW by using low expenditure of power per ton of recovered product.

Another object of the present invention is to provide an apparatus for recovering cellulose fibers from the light weight fraction of MSW which overcomes the disadvantages of the prior art.

Another object of the present invention is to provide a coordinated continuous machine for recovering cellulose fibers directly from the light weight fraction of MSW.

Another object of the present invention is to provide an apparatus capable of classifying mixed feedable materials of differing weights.

Still another object of the present invention is to recover a classified high test cellulose fiber from the light weight fraction of MSW for use in fiberboards, building boards and molded cabinets, cases, pallets and the like.

A further object of the present invention is to provide a fiberized cellulose suitable for direct recycling to make commercial grade folding boxboard and other paper pulp products such as paper tubes, egg cartons and the like.

Another object of the present invention is to provide a substantially glass free defibered cellulose feed for manufacturing into products demanding a low ash content including relatively high BTU Fuel Products.

Another object of the present invention is to provide a high purity plastic recovered from MSW.

Other objects, aspects and advantages of the present invention will be apparent from the detailed description and the accompanying drawings.

The present invention provides a process and apparatus for difficult recovery of a cellulose paper product from a contaminated paper-plastic mixture by exposing the mixture to controlled wetting to increase the weight of the paper component; subjecting the wetted mixture to reduction forces to fiberize and refine the paper component and then separating the wet, fiberized paper from the plastic and other contaminant.

In addition, the invention provides a cellulose product recovered from MSW having a high cellulose content suitable direct repulping to paper; a plastic product of high plastic content, and a mixed plastic-paper product of low ash content which is suitable for use as a clean fuel.

While this invention has utility in separating any paper-plastic mixture it has particular utility when the infeed is the light weight fraction of MSW which has been chopped to a size of between 2" to about 6". A controlled amount of fluid is added to the chopped paper-plastic mixture which is preferentially absorbed by the paper.

Controlled amounts of water are added as required to the paper-plastic mixture either by a spray shower in a tumbler, or by other suitable means. The water is then more rapidly absorbed by the paper fractions making the paper portions substantially heavier than the plastic and prepared for separation. A separating means is provided to separate the prepared heavier papers from the remaining mixture.

An effective separation according to the process of the subject invention has been achieved by feeding treated mixtures into a rotor chamber in which the paper is classified and separated from the paper-plastic mixture by subjecting it to a fluidized centrifugal zone of treatment wherein such zone contains rotor chambers provided with low pressure air means to create a low air pressure area within a portion of the rotor chamber. The specific gravity differentials between the paper fractions and the other components are exaggerated under centrifugal forces, and controlled air streams.

When the wet paper-plastic mixture is subjected to this fluidized centrifugal zone, the paper tends to promptly fiberize resulting in smaller refined particles of paper. This further aids in separation of paper fibers from plastics since there is no corresponding reduction in the size of the plastic film, foam, or sheets which remain oversized.

A cylindrical rotor chamber is employed to form the fluidized centrifugal field. The rotor chamber has rotor blades acting as a fan throughout its length. A classifier screen surrounds the rotor blades and is dimensioned for passage of the reduced fiberized paper.

A blower and suitable duct means are provided below the rotor to channel high velocity air past the bottom of the rotor to create further low pressure areas within the rotor zone thereby providing a downward suction on the plastic and oversize feed as it falls through the rotor chamber and into the discharge air stream.

The paper-plastic mixture preferably the light fraction of MSW is chopped to a size of between 2" and 6" and treated with a controlled amount of water. This wetted mixture is then fed continuously into the top of the rotor chamber. The spinning fan blades impact the feed against a classifier screen. During this process, the wet paper becomes fiberized which results in the paper breaking into cellulose fibers of a sufficiently small size to pass through the screen openings. There is no corresponding reduction in the size of the plastic fraction. The openings in the classifier screen are dimensioned especially for the passage of paper fractions. When the mixture is fed into the rotor, the moisturized paper is preferentially

ejected through the classifier screen while plastics and oversize contaminants clear through the rotor chamber into the discharge air stream.

The preferred embodiment of the present invention is illustrated in the drawings. However, it should be expressly understood that the present invention should not be limited solely to the illustrative embodiment. As for example, the uniform treating and feeding, two stage presizing and reduction, two or three stage dispersion of moisture and additives, and the removal of a variety of contaminants within the rotor classification zone all are contemplated to be within the scope and purview of subject invention.

## DESCRIPTION OF THE DRAWINGS

FIG. 1 is a block diagram of the preferred embodiment of the subject invention.

FIG. 2 is a side elevational view of the apparatus of this invention.

FIG. 3 is a bottom plan view of the rotor chamber shown of FIG. 2.

FIG. 4 is a top plan view of the rotor chamber shown of FIG. 2.

FIG. 5 is a side view of the rotor chamber shown in FIG. 2.

FIG. 6 is a side elevational view of another embodiment of the present invention.

## DETAILED DESCRIPTION OF THE INVENTION

The process of the invention can be best followed with reference to the block diagram of FIG. 1. The light weight fraction of MSW, that is MSW in which the primary steps of crushing and shredding or other separation means such as screening and chopping have been performed to remove substantially all the heavy material as well as metals and which is substantially free of heavy materials, such as stones, iron, or other metal objects, glass, carpeting, construction debris, wire, rope, rubber, tires and white goods is continuously fed to a feed conveyor 6 which feeds the LW-MSW to a paper cutter 8 which cuts the LW-MSW to a size of about 2 inches. The chopped material is then fed to a head box 10 which is a container having a belt conveyor 16 at the bottom and is adapted to feed a metered amount of LW-MSW to the first stage rotor chamber 18. There are optional water showers 17 at the top of the head box to control the moisture content of the infeed and for dust control purposes. The LW-MSW is then fed to a first rotor chamber 18 which subjects the LW-MSW to a ballistic attrition wherein glass, grit, paper embedded with sand and degraded or short fibers or those that are saturated or contaminated are separated from the mix. This preliminary attrition stage separates and classifies gross contaminants from the plastics and high strength papers based on particle size and the action of the rotor creates centrifugal forces which cause heavier particles to fly through the classifier screen 22. Such heavier particles include glass, grit, degraded vegetable matter and heavily contaminated papers which become further degraded and discharged. The remaining LW-MSW portion falls through the rotor chamber 18 into the moisture control chamber 32. Any means of introducing a controlled amount of moisture is acceptable such as spray showers 35 introducing a controlled amount of moisture with a chute or tumbler.

Conventional moisture sensors 33 monitor the moisture content of the feed. Moisture differential is a significant, aspect of this invention. This process is controlled semi-dry process for the classification of fiberized cellulose fibers from contaminated paper-plastic mixtures.

The average paper content in LW-MSW is generally between 45 and 65% by weight. The remainder of

the feed contains large amounts of plastics. The initial moisture content of the LW-MSW generally ranges between 10% and 35% EMC (equilibrium moisture content) by weight oven-dry basis. According to this invention the moisture content of the feed to the rotor chamber 38 is usually raised by 3 to 10% by weight. Preferably the moisture of the feed as it enters rotor chamber 38 should be between 20% and 35% EMC oven-dry basis and most preferably at 25%. It should be noted that during the first rotor chamber treatment the feed dries considerably; thus, it is usually possible to process in the second rotor chamber at the optimum moisture content even if the feed was initially somewhat wetter than 25%. If the moisture content of the feed to the first rotor chamber 18 is less than 15%, an initial adjustment is made in the moisture content by liquid addition to increase the moisture content to the first rotor chamber to 18 to 20%.

It should be further noted that if the feed is composed of heavy papers such as Kraft that a higher average moisture level would be desirable. This factor is attributable to the great absorbancy of the flutes corrugated medium containing short fibers, and the non-absorbancy characteristics encountered in fiberizing heavy kraft liners.

When the moisture content is too low, the yield of recovered paper decreases. If the water content is too high the LW-MSW tends to clog classifier screens. Thus, although the 15% to 35% range is optimum for most plastic paper mixtures derived from MSW, the yield vs. clogging tendencies of the feed are monitored. As indicated above, where there is a high percentage of heavy paper, such as Kraft paper, the moisture content may reach up to 60% of paper moisture content by weight.

The rate of moisture absorption of the paper results in a marked differential between the paper components and weight of other materials in the feed, especially the plastic. The moisture treated LW-MSW is fed by suitable feeding means such as a chute or conveyor 36 to a second rotor chamber 38 which subjects the moisture treated LW-MSW to a fluidized centrifugal field causing rapid separation of the wetted paper. The wetted paper begins to fiberize quickly in the rotor chamber 38 due to the attrition action thereby becoming smaller in size than the remaining plastics, textiles, tapes, and other contaminants, and thus facilitating separation. A classifier screen surrounds the second rotor chamber and is selectively dimensioned for the passage of particles of fiberized paper. Thus the cellulose fibers and paper particles are removed through the classifier screen 40. The accepted classification product is then bailed and shipped to paper mills for direct repulping and reuse.

A blower 42 supplies a high velocity air stream across the bottom of the rotor chamber at an angle of about 90.degree. to the axis of the discharge of the rotor chamber. This air stream creates an adjustable low pressure area under and within the rotor chamber 38 thus preventing the lower chamber from acting as an upward air intake. Thus the air flow through the rotor is carefully controlled from the infeed at the top and out through the openings in the classifier screen 40.

The construction of this invention can be more particularly understood in reference to FIGS. 2 to 6. As shown in FIG. 2, infeed head box 10 which is a rectangular container of sufficient size to prevent surging in the first rotor chamber is provided. A size of from 10 to 25 feet in length and 3 to 6 feet wide and 6 to 10 feet has been found sufficient for a rotor chamber of about 36 in. diameter. In-feed rakes 12 and 14 are provided in head box 10 to move a metered amount of feed along conveyor 16 which is located at the bottom of head box 10 and which delivers the feed to the inlet of rotor chamber 18. Rotor chamber 18 is a cylindrical unit. The diameter and the height of the rotor chamber can vary depending on the amount of feed per hour to be processed.

As best seen in FIGS. 5 and 6, the rotor chamber 18 contains a rotor assembly 19. The rotor assembly 19 contains rotor blades 20 and 21. The blades may vary in thickness from about 1/16 of an inch to 1 inch. Preferably in the treatment of MSW, the blades are from 3/16 of an inch to 3/4 of an inch thick and are

preferentially from 1/2 to 3/16 of an inch thick. The number of rotor blades can vary and are dependant on the amount of feed processed per hour, the diameter of the rotor chamber and the speed or RPM of the rotor assembly. For a rotor chamber from 36" to 48" in diameter to 8 to 12 sets of parallel rotor blades 20 and 21 spinning at 1000 RPM blade tip speed can be used to process from 14-20,000 lbs per hour of LW-MSW. Two of the rotor blades 21 are shorter than the remaining rotor blades 20 to facilitate feeding into the rotor chamber. There are preferably eight rotor blades in each set. Here again, the number of rotor blades may be varied depending on the desired condition of the feed to be processed. It is contemplated that a variety and greater or a lower number of blades can be used within the scope of the invention. Each set of rotor blades 20 and 21 is propelled by a rotating shaft and secured by a cap, nuts, and flanges in a conventional manner. The rotor core 25 contains air holes 26 for controlled passage of air into the rotor chamber 18. The rotor core contains slots 28 to direct additional air from within the interior of the rotor housing perpendicular to the exterior of the rotor chamber. Optional cutting members 30 which are long sharp vertically spaced blades are located in the interior of the rotor chamber adjacent to the classifier screen 22.

A classifier screen 22, preferentially made of rolled steel, is perforated and welded in a cylindrical pattern surrounding the rotor blades. Duck work further surrounds the classifier screen to form a discharge chute 24 from the rotor chamber. The dimensions of the classifier screen varies with the diameter of the rotor chamber. For example, in a 36 inch diameter rotor chamber it might be considered optimum to employ a classifier screen about 24 in. high. However, such dimensions are entirely determined by the nature of the materials which may be treated by the classifier described herein. The openings in such classifier screen may also be diverse both in size and shape; for example, in the first rotor chamber 18, the openings are normally 1/4 inch round holes when processing LW-MSW, but these may be readily adjusted to smaller or larger holes or any different configuration of openings to permit the passing of the materials out of the rotor chamber without blinding. The classifier screen 22 is situated so that there is usually no metal to metal contact between the rotor blades 20 and 21 and the classifier screen 22. Air jets (not shown) may be provided at the exterior of the rotor chamber to direct high pressure air through the discharge duct work in the event there is any blocking.

During operation of the rotor chamber the rotor blades 20 and 21 act as a fan to draw in controlled air which is then directed through slots 28 toward screen 22. The LW-MSW is spun in the chamber against the screen 22 and the cutting blades 30. The heavy small particles fly through the screen 22 and are thus removed from the system, while papers, plastics, and oversize particles are retained for coordinated treatments to complete the classification process.

The processed LW-MSW from rotor chamber 18 has been found to be a good fuel. Thus although it is preferred to process the LW-MSW further to recover the paper fiber, the product of rotor chamber 18 can be immediately used as a low ash fuel.

Discharge chute 24 feeds the classified product from the bottom of rotor chamber 18 into tumbler 32. Fan 23 is located at the side of rotor chamber 18 near the bottom to propell the pressured feed into tumbler 32. Tumbler 32 is a conventional rotary tumbler having showers 35. The LW-MSW is treated with water and other additives by the spray from the showers 35. Moisture content of the LW-MSW is monitored at the tumbler. Sufficient water is added through shower 35 to raise the paper moisture content about 3%-10% by weight and preferrably the paper moisture content of the LW-MSW will be raised to about 25% by weight. Preferrably other additives are incorporated at the tumbler 32. Wetting agents such as ethylene glycol, Igapel, or ZonylA made by DuPont, which reduces surface tension of paper and increases the absorbancy of the paper are added as desirable. In addition detergents and deformers which also promote rapid fiberization of paper components are added to the system. A variety of brightness and paper deinking agents may also be optionally dispersed on the feed.

The wetted LW-MSW is fed by chute 34 to belt conveyor 36. Belt conveyor 36 delivers the LW-MSW to the top of rotor chamber 38. Rotor chamber 38 is similar to rotor chamber 18 except that a suitable blower 42 supplies high velocity air between 4,000 and 10,000 CFM at the bottom of second rotor chamber 38, preferably at an angle of 90 degree to the axis of the discharge through the rotor chamber 38. As shown in FIG. 5, a venturi means 44 is optionally provided across the path of the air outlet from the blower 42. During the operation of the second rotor chamber, the blower 42 creates a controllable low pressure region at the lower portion of the rotor chamber to provide a downward force on the descending plastics and oversize LW-MSW. In addition, this high velocity air across the bottom of the rotor chamber prevents the lower rotor chamber from acting as an upward air inlet and furthermore, clears the rotor chamber of rejects and prevents blinding from plastics while sweeping the system clean by sucking materials into the discharge air stream and causing a drying effect on the plastics.

Paper fibers are collected through chute 46 passing through screen 40, and are then sent to a bailing station not shown. Screen 40 is identical to screen 22 including the optional cutting bars except for the holes or openings in the screen. The screen 40 has preferably somewhat larger holes than does the screen 22, preferably about 1/2 inch, smooth edged chauffered holes, although these openings may be adjusted to meet a variety of classification requirements.

The rejected material exists through chute 45 from which it is delivered by suitable means such as a conveyor to a cyclone air classifier 43 of conventional design. The heavy portion is then recovered from the cyclone air classifier and returned to conveyor 36 for recycling in rotor chamber 38. Optionally, water showers (not shown) may be included to bring the moisture content of this heavy paper fraction back to optimal levels before recycling. An electrical moisture sensing means (also not shown) may optionally be used to detect moisture contents since there are significant moisture losses which occur at each stage of the system.

Between 40 to 60 percent by weight of the available paper on a dry basis of the feed is recovered by use of this process. The recovered paper product of the LW-MSW is suitable for the direct repulping into valuable commercial grades of paper fibers.

The plastic produced from cyclone 43 is about 70% plastic and is a valuable plastic product.

In another aspect of this invention, industrial waste which is composed primarily of cardboard, tape and other packing material and which has a very high Kraft Content is chopped and fed into the first rotor chamber 18. The feed is initially wetted to an EMC of 30 to 40%. During the first rotor chamber treatment, the short paper fibers absorb the added water and are ejected through the first classifier screen 22. The product of rotor chamber 18 enters moisture control chamber 32. Additional moisture is added at 32 where the moisture content is restored to about 25%. In addition, detergents and other wetting agents are added which cause the long Kraft Paper to fiberize the rotor chamber 38.

The fiberized Kraft Paper is recovered through screen 40 while the tape and other light weight contaminants fall to the bottom of rotor chamber 38. The recovered product has a high concentration of Kraft fibers which are long length and high strength fibers. This product is more valuable because of the concentration of long length Kraft fibers and can be directly repulped into Kraft linerboard and Kraft packaging.

Another embodiment of the present invention is shown in FIG. 6. FIG. 6 depicts a vertically stacked single shaft classifier. Here, the LW-MSW is fed into the first rotor chamber 18A through a head box or other suitable feeding means. The first rotor chamber 18A is stacked on top of the second rotor chamber 38A such that the classified feed from 18A falls directly into the second rotor chamber 38A by gravity. Spray showers 48A are provided to allow the addition of the water and other additives such as

detergents and wetting agents directly to the classified product of rotor chamber 18A. Thereafter, the LW-MSW is fed by gravity into rotor chamber 38A. Charging port 50A is provided intermediate rotor chamber 18A and 38A to allow recycling of the feed as described in the other embodiment of this invention. Blower 42A is located at the bottom of rotor chamber 38A and functions are described above. Rotor blades in rotor chamber 18A and 38A are driven by a single shaft 52. A single cylindrical casing 52A prevents the loss of any of the feed during its flow from the first rotor chamber 18A to the second rotor chamber 38A.

During operation of this apparatus, the high density, fine fractions are first separated through classifier screen 22A and ejected out through exit 23A. The classified product of rotor chamber 18A falls directly into the additive treating section 32A. Here, the remaining LW-MSW is sprayed with water and other additives to effect optimum moisture and related chemical adjustments in accordance with the invention. The LW-MSW then spirally feeds by gravity at a continuously metered rate into rotor chamber 38A. The classified cellulose fibers spin through the classifier screen 40A and thereafter collected through chute 46A. Paper fiber may be bailed for direct shipment to the paper mill. For maximum paper recovery, the remainder exists through chute 45A and can optionally be grossly separated in cyclone filter again employing my moisture differential and heavy paper portions recycled directly to the showers or my stage 2 rotor chamber.

#### EXAMPLE 1

5,000 lbs of the light weight fraction of MSW, from the town Brockton, Mass. from which the heavy fraction had previously been removed by a primary shredder and fed into a rotary magnet and through a rotary screen; was chopped to a size of between 2" and 6". The LW-MSW had the following composition:

Description	Percentage
Glass grit and stone	3%
Non ferris metals	1%
Rags and textiles	4%
Film plastics	14%
Hard Plastics	2%
Wood	1%
Vegetable matter	3%
Water	10%
Paper	62%

Approximately 700 lbs of water was added to the infeed by a water shower along with 50 lbs ethylene glycole as additive. The partially wet LW-MSW was then fed to the first rotor chamber which was 18 inches in diameter and contained 80 rotor blades.

The blades were driven at 1500-2500 rpm. The LW-MSW product of the first rotor chamber was then treated and tumbled wherein 750 lbs. of water was added. The wet LW-MSW was then fed into a second rotor chamber 18 inches in diameter having 80 rotor blades spinning at 1200-1800 rpm 2300 lbs air dry recovered paper product was collected through the second stage classifier screen. It was directly



repulped in a Connecticut paper mill and used on a production paper machine to make excellent grade fiber board for folding cartons equal to or better than present commercial grades. The recovered paper contained less than about 2% plastic and approximately 3% ash content by weight with approximately 84% of the fiber when repulped holding on a 100 mesh screen as opposed to only 74% of the normal commercial paper pulp holding on a 100 mesh screen.

## EXAMPLE 2

### Old Corrugated Boxes

Old corrugated boxes, a leading commodity in the secondary fiber industry, are normally obtained from super markets and shredded by paper stock dealers, while some old corrugated may be derived from sources such as container manufacturers selling trims and edge clippings as developed in volume. Such trim and edge clippings are to be preferred. However, it is important that boxes as in old corrugated boxes must be shredded to a small size prior to introduction to two-phase classification and prepulping treatment of such used paper stocks. Chopping and shredding is important in that the size of this must be reduced to a particle size of approximately two to three inches. Strips in widths of about 2" by long lengths may be acceptable to feeding as these are quickly broken into proper lengths at the first stage. The purpose of such old corrugated secondary fiber processing is two fold: to reduce horsepower consumption at the pulper, in the paper mill, and to reduce the usual long fiber reduction cycles for Kraft. These cycles frequently approach one hour in batch-pulpers and employ excessive horsepower in the early phase of wet pulp reduction; and to eliminate undesirable short fiber fractions prior to any paper mill pulping in order to obtain improved long fiber kraft pulps. Elimination of the corrugated fluted medium a short-fibered material having deleterious and negative values, when recycling of old corrugated, is a special advantage. Proceeding with small batches of previously chopped up pieces of old corrugated boxes as received at the paper mill in random samples, my test materials were soaked under extremes of moisture conditions. It was observed that water was shed from the surfaces of the outside liners as these hard surfaces frequently were water-resistant. However, moisture was rapidly absorbed by the corrugated fluted medium and such medium became promptly softened. In fact, the entire laminate of the wet corrugated board consisting of a top liner became easily delaminated often prior to introducing to the test classifier. The first stage of the classifier action was important at this treating zone where the wet short fiber medium was extracted through the 1/4" screen plates and separated from the Kraft liners. The liner portion of long-fibered Kraft paper was retained in excellent condition for the on-going second stage whereby the oversize pieces were vigorously flexed and chopped to a size to pass through the 1/2" second-stage screen. Thus, 80 to 85% of a uniformly processed Kraft fiber product was retained having high physical and mechanical properties. Oversized pieces which did not yield to the treatment as described in stage one were rewet and recycled in the same system. The reject fraction of the first stage, 12% to 15% by weight, was collected separately for use with other grades of paper or paperboard. Net overall losses in the system were less than 5% by weight from tapes and extraneous contaminants. The cycle times for Kraft re-pulping were reduced up to 50%, and effluent pollution significantly improved.

## EXAMPLE 3

### Experimentation Examples

#### Old News:

A series of tests employed old newspapers for purposes of reduction of ink contaminants, prior to de-inking of such old newspapers and restoration of the ground wood fiber. Fifty pounds of mixed newspapers, mostly newsprint with some coated inserts, were employed for these trial batches. The



newsprint was reduced in size more quickly by the first rotor, especially after adding 10%-12% moisture to bring up the moisture content to about 20%. At lower levels of moisture, the inks would not release as quickly and effective scaling of surfaces with minimum loss of fibers was substantially improved at moisture levels of 25%. However, this was balanced by losses in fiber and an optimum moisture content was found to be at 18% to 22% O.D. basis. Ink removal was observed to be at an estimated 40-50% of print on surfaces of the old news. Printing inks were initially removed through flaking off and by scraping the paper against the sharp edges of holes in the screen plates. Incidental fiber losses were in direct proportion to the moisture content. In addition to removal of inks, fiber structures were opened and substantially exposed for purposes of improved dispersion and brightening. The second stage classification through the 1/2" screen provided a consistent and uniform size particle advantageous for optimum de-inking and/or bleaching controls without oversized extraneous materials present. Coated and wet strength papers are a frequent cause of contamination in news. However, my method, as described in these experiments, also provided visible destruction of surface coatings to a degree which permitted many ground wood coated stocks to be prepared with a minimum of contamination. The brightness of the old news was quickly increased through my pre-pulper classification stages to 40-45 Brightness from original levels of about 30 Brightness in these experiments.

A number of mixed ground wood and old news test samples were employed for experimental re-pulping and de-inking. A method of pulping was devised and demonstrated at the laboratories of Bolton-Emerson Pulp and Paper Research Center, Lawrence, Mass., whereby commercial detergent was added directly to the pulper to clean the fiber and develop a controlled foam. The brightness of such pulps from old news improved immediately. With this amplification of flotation removal of foam from the surface of pulper stock, a modified flotation repulping was accomplished using the pulper stock flows. The brightness of such old newsprint pulps reaches about 52 Brightness. However, improved brightness of up to 60 or better was obtained on repeated flotation treating for improved de-inking employing an added 2% hydrogen peroxide. This modified flotation method as disclosed hereby yielded a high brightness fiber fully suitable for newsprint. Losses in the prep-pulper classification stage were 12%. However, additional losses occurred through repulping with flotation using detergent de-inking as noted. The latter averaged an additional 18% to 20% loss of fiber with removal of foam laden inks as skimmed from the surface of the pulper using a deflector to a discharge port.

It should be understood by those skilled in the art that wide and various modifications may be made in my present invention without departing from the intent and are specifically the scope thereof, as described in the specification and defined in the appended claims, as described in the specification and defined in the appended claims, and used in demonstrations and commercial practice in production plants at the numerous waste resources recovery facilities at Brockton, Mass. for the recovery of the commercial grade paper product shown here having technical characteristics in keeping with the specific objectives of quality through my techniques as disclosed herein constituting a new process in the conversion of garbage into process of paper fibers. My invention may be used for further classifications of materials having diverse industrial and agricultural usage when upgraded through my process techniques altogether encompassed within the scope of these inventions disclosed herein.

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<u>4278539</u>	Jul., 1981	Santhanam et al.	423/140.
<u>4298456</u>	Nov., 1981	Coombs et al.	210/695.
<u>4342640</u>	Aug., 1982	Lewis	208/251.
<u>4388179</u>	Jun., 1983	Lewis	208/251.
<u>4541920</u>	Sep., 1985	Seiuer	208/251.
<u>4541924</u>	Sep., 1985	Rosensweig	208/251.
<u>4588507</u>	May., 1986	Saudray et al.	210/695.

#### Foreign Patent Documents

2854949	Jul., 1980	DE	210/695.
2536088	May., 1984	FR	423/140.
0067703	Jun., 1978	JP	208/251.
0030787	Feb., 1982	JP	208/251.
0101193	Jun., 1983	JP	208/251.
0973484	Nov., 1982	SU	423/151.

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#### *Parent Case Text*

This is a continuation of application Ser. No. 860,542, now abandoned, filed on May 7, 1986.

#### *Claims*

What is claimed is:

1. A method for decreasing the pressure drop in a fixed bed hydrogenation plant which comprises treating an atmospheric or vacuum distillation residual oil containing 5 ppm or more of iron content by the use of a high gradient magnetic separator under conditions of the strength of the magnetic field being from 500 to 25,000 gauss, the temperature being from room temperature to 400.degree. C., and the linear velocity being 0.1 to 50 cm/second, and thereafter hydrogenating said magnetically treated oil in a fixed-bed hydrogenation plant.
2. A method according to claim 1 wherein said oil is brought into contact with a gas containing hydrogen sulfide or a gas containing hydrogen sulfide and ammonia to convert the soluble iron content contained in said oil into insoluble iron compounds, and the latter are then treated by said high gradient magnetic separator.
3. A method according to claim 1 wherein said high gradient magnetic separator is an electromagnet separator or a permanent magnet separator.
4. A method according to claim 1 or 2 wherein said strength of the magnetic field is 1 to 20,000 gauss, the temperature is from room temperature to 250.degree. C. and the linear velocity is 0.2 to 20

cm/second.

5. A method for decreasing the pressure drop in a fixed-bed hydrogenation plant which comprises treating an atmospheric or vacuum distillation residual oil containing 5 ppm or more of iron content by the use of a high gradient magnetic field under conditions of the strength of the magnetic field being from 500 to 25,000 gauss, the temperature being from room temperature to 400.degree. C. and the linear velocity being 0.1 to 50 cm/second, and feeding said magnetically treated oil to a fixed-bed hydrogenation plant for the hydrogenation treatment.

6. A method according to claim 5 wherein said petroleum oil fraction is brought into contact with a gas containing hydrogen sulfide or a gas containing hydrogen sulfide and ammonia to convert the soluble iron content contained in said petroleum oil into insoluble iron compounds, and the latter are then treated by said high gradient magnetic separator.

7. A method according to claim 5 wherein said high gradient magnetic separator is an electromagnet separator or a permanent magnet separator.

8. A method according to claims 5 or 6 wherein said strength of the magnetic field is 1 to 10,000 gauss, the temperature is from room temperature to 250.degree. C. and the linear velocity is 0.2 to 20 cm/second.

9. In a method of hydrogenating an atmospheric or vacuum distillation residual oil in a fixed-bed hydrogenation plant, the improvement which comprises employing as the hydrogenation reactor feed an atmospheric or vacuum distillation residual oil which, containing 5 ppm or more of iron content, was subjected to high gradient magnetic separator under conditions of the strength of the magnetic field being from 500 to 2500 gauss, the temperature being from room temperature to 400.degree. C. and the linear velocity being 0.1 to 50 cm/second.

10. The method of claim 9 in which said distillation residual oil was contacted with a gas containing hydrogen sulfide or a gas containing hydrogen sulfide and ammonia to convert the soluble iron content contained in the distillation residual oil into insoluble iron compounds prior to treatment in said high gradient magnetic separator.

11. A method according to claim 9 in which said high gradient magnetic separator is an electromagnetic separator or a permanent magnet separator.

12. A method according to claims 9 or 10 wherein the strength of the magnetic field was 1 to 20,000 gauss, the temperature was from room temperature to 250.degree. C. and the linear velocity was 0.2 to 20 cm/second.

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### *Description*

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## BACKGROUND OF THE INVENTION

### (1) Field of the Invention

The present invention relates to a method for removing the iron content contained in a petroleum series mineral oil fraction.

## (2) Description of the Prior Art

In the industrial field of petroleum refining, generally a crude oil is fractionated to separate it into a gasoline fraction, a kerosene fraction, a gas oil fraction and an atmospheric distillation residual oil fraction. These petroleum hydrocarbon fractions can be each refined to make petroleum products such as gasoline, kerosene, gas oil and fuel oil. A refining process which is now employed most usually is the so-called hydrogenation refining process in which hydrogen is allowed to react with the petroleum hydrocarbon fractions in the presence of a catalyst under a high pressure at a high temperature.

Impurities present in the petroleum fraction which is a raw material for the hydrogenation refining process contain or an extremely low concentration (e.g., 1 ppm or less) of iron content, when the petroleum fraction is a distillate fraction. However, the raw material distillates containing an iron content as much as 1 ppm or more are prepared on occasion, and some of such material oils contain 100 ppm or more of the iron content.

In many cases, such a material oil has a high acid value, and thus at least a part of the iron content contained therein can be considered to be that which is dissolved in the oil as a result of corrosion in a distilling plant, a storage tank for the distillate, oil transport pipes and the like by acidic materials present therein.

When such a material containing the higher iron content is treated by the hydrogenation refining process, a troublesome problem will occur in the operation of a refining plant. That is, since they are dissolved in the material oil, compounds containing the iron content are not caught by a filter disposed an inlet of the plant, get into the plant, and reach the reactor which is an important portion of the plant, where the compounds are decomposed due to chemical reactions. The iron content is deposited in the form of sulfides between catalytic grains in the reactor and clog the reactor or to adhere to the surfaces of the catalytic grains, with the result that the power of a catalyst will be lowered. In the case that such a material oil is treated, the distilling plant, the distillate storage tank, the pipes and the like are manufactured with anti-corrosive materials, or alternatively the insides of these members may be subjected to a lining treatment with anti-corrosive materials, as known. In this measure, however, it is necessary to give the anticorrosion treatment to the huge storage tank and the long oil transport pipes, which increases costs.

As another process, a guard reactor is disposed upstream of the reactor in the hydrogenation refining plant.

In this arrangement, the material oil is introduced into a reactor which is called the guard reactor, where the iron content dissolved in the oil is decomposed by chemical reactions. The iron content is then changed into sulfides, and the latter are caught by a filler and catalytic grains with which the guard reactor is filled, and are deposited in the guard reactor.

The material oil from which the iron content has been removed in this way is caused to leave the guard reactor for the reactor.

According to this process, the clogging of the reactor and the deterioration in the used catalyst can be prevented, but the clogging of the guard reactor and the decline of the catalyst, by the iron compounds, with which the guard reactor is filled are unavoidable.

Still another process is composed of treating the distillate containing the iron content with an aqueous sodium hydroxide solution to neutralize the acidic materials present in the oil and extracting them into an aqueous solution.

In this process, the iron content is in the form of hydroxides or oxides, and the latter are transferred into the aqueous solution or are collected on each interface between the aqueous solution phase and the oil phase. This process is now utilized as a manner for extracting naphthenic acid from the petroleum fraction containing the acid. If the recovered naphthenic acid has any commercial value, the above mentioned process is advantageous.

However, this process is not practicable for a high-viscosity oil because of the difficulty of the separation between the oil phase and the aqueous solution phase and poor extraction of a naphthenate into the aqueous solution, although it is not impossible when a viscosity of the material oil fraction is low, for example, as in the case of a spindle oil fraction.

As still another process, the petroleum series mineral oil is brought into contact with hydrogen sulfide or ammonia in order to convert the iron content in the mineral oil into iron compounds which are insoluble in the oil, and the thus formed iron compounds are then removed by filtration, centrifugation or the like. However, particles deposited in the petroleum series mineral oil principally have a particle diameter of 10 microns or less, or a much small particle diameter than 1 micron on occasion. In consequence, the usual fine mesh filter cannot catch and remove such particles. One can consider making use of a membrane or a filter paper, but in the treatment of a great deal of the petroleum series mineral oil, such a material will be clogged with the particles to increase pressure and to break it, and additionally troublesome exchange is necessary. In short, such a material as the membrane or the filter cannot be employed on an industrial scale, though its employment is possible on a laboratory scale. Further, a method of using the technique of centrifugalization is also present, but it is not practicable either from the viewpoints of structure and operation.

On the other hand, the atmospheric distillation or the vacuum distillation residual oil contains, as the iron content, a large number of fine particles comprising iron and/or iron compounds. These iron particles are those which have come from a tank, pipes and a plant owing to erosion, when the crude oil is transported from a producing center by a tanker, is then stored in the tank, and is afterward delivered to the distilling plant via the oil transport pipes.

If such a distillation residual oil is used as the material oil for a fixed-bed type hydrogenation plant, the fine iron particles contained in the material oil will be deposited on the catalyst or between catalytic grains in a reactor, so that the latter will be clogged therewith or an activity of the catalytic grains will declined. Particularly, in the case of the clogging of the reactor, the pressure in the plant will be thereby increased, and at times, the operation of the plant must be stopped, which fact will give rise to an extremely large economical loss.

It is thus apparent that if the fine particles comprising the iron content are removed from the material oil, a great advantage will be obtained. However, such fine particles are as extremely small as about 0.1 to about 20 microns and thus cannot be removed by a filter which is generally employed in the petroleum refining industry.

In addition to the above mentioned techniques, several other processes for removing the fine particles can be enumerated. For example, a filter paper or a membrane having a fine mesh can be used as a filter. In the case that such a filter is employed, however, the pressure loss is very large, and clogging is liable to occur, which facts scarcely permit the filter to be used for a long period of time. In addition, since it is necessary that the old filter is exchanged for a new one, the manner of using the filter is indeed unsuitable for the treatment of a large amount of the material oil from the viewpoint of the operation.

Another method is characterized by the employment of centrifugalization, but it is poor in throughput in

view of structure and operation and consequently is less practicable.

## SUMMARY OF THE INVENTION

The inventors of the present application have intensively researched with the aim of solving the above mentioned problems, and as a result, it has been found that the iron content can be separated by the use of a high gradient magnetic separator, and what is better, the treating power is very high. On the basis of this finding, the present invention has been completed. That is, the present invention is directed to a method for removing the iron content in a petroleum series mineral oil which comprises treating a petroleum series mineral oil fraction containing 5 ppm or more of said iron content by the use of a high gradient magnetic separator under conditions of a magnetic field strength being from 500 to 25,000 gauss, a temperature from ordinary temperature to 400.degree. C., and a linear velocity of 0.1 to 50 cm/second.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1 to 3 attached hereto are flow sheets illustrating methods of the present invention.

## DETAILED DESCRIPTION OF THE INVENTION

Materials used in the present invention are petroleum series mineral oils containing 5 ppm or more of iron content. This iron content means iron and/or compounds soluble in the mineral oil and fine particles of iron and/or iron compounds therein, as described above.

The petroleum series mineral oils to be treated by the present invention include a variety of petroleum series crude oils, various distillates obtained by distilling the crude oils under ordinary pressure or a reduced pressure, and these fractions which have been subjected to a solvent dewaxing treatment.

The present invention will be more useful, when relatively heavy fractions each having a 10% running point of 280.degree. C. or more in terms of ordinary pressure are treated.

Further, the present invention is effective in the case that a distillate oil prepared by distillation is directly subjected to the treatment of the present invention without undergoing the above mentioned refining treatment.

The objects of the treatment by the present invention are the mineral oil fractions containing a small amount, for example, 1 ppm to a relatively large amount, e.g., about 500 ppm, in general, 5 to 200 ppm, of a soluble iron content.

Generally, some of the crude oils produced in South America contain the iron content in a relatively large amount, and thus the mineral oils from these materials can be treated effectively by the present invention.

Moreover, the petroleum series mineral oils used in the present invention include atmospheric or vacuum distillation residual oils prepared by an atmospheric or a vacuum distillation of various petroleum series crude oils, deasphalting oils of these fractions, and the like.

These distillation residual oils contain a great deal of impurities such as metals, for example, iron, nickel, vanadium; sulfur, nitrogen and/or asphaltene.

These distillation residual oils will be contaminated with fine particles comprising iron or iron

compounds ( $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$  and the like) during transportation and storage. Such fine particles will be concentrated in the distillation residual oil, and the concentration of the iron fine particles in the residual oil will become as high as 10 to 100 wt ppm sometimes. The diameter of each fine particle ranges from 0.1 to 100 microns, but much of the fine particles have as small diameters as 20 microns or less.

A high gradient magnetic separator used in the present invention is a magnetic separator which is designed so as to separate paramagnetic fine particles from weak paramagnetic fine particles or diamagnetic fine particles. In the high gradient magnetic separator, a ferromagnetic filler is first placed in a uniform high magnetic field space, and a magnetic field is then generated therein so that a magnetic field gradient as high as  $10^3$  to  $20,000 \times 10^3$  gauss/cm may occur usually around the filler, whereby the ferromagnetic or the paramagnetic fine particles are magnetically attracted on the surface of the filler. In this way, the ferromagnetic or the paramagnetic fine particles are separated from the other fine particles.

As the above mentioned ferromagnetic filler, there can be used a mass of ferromagnetic small-gage wires such as steel wool or steel net, each unit material of which usually has a diameter of 1 to 1,000  $\mu\text{m}$ , or an expanded metal or steel beads. Above all, the expanded metal or the steel beads are preferred.

As the high gradient magnetic separators, there are an electromagnetic type in which the uniform high magnetic field is generated by an exciting coil, and a permanent magnet type in which the uniform high magnetic field is generated by a permanent magnet. An example of the electromagnet type high gradient magnetic separator is SALA-HGMS (registered trademark) manufactured and sold by Sala Magnetic Incorporated in U.S.A.

Now, a method of the present invention will be described.

The method for removing the iron content in a petroleum series mineral oil fraction by the use of a high gradient magnetic separator comprises introducing the mineral oil fraction into a magnetic field space in the high gradient magnetic separator and magnetically attracting the iron content by a ferromagnetic filler placed in the magnetic field space in order to remove the iron content therefrom.

Variables for the operation of the high gradient magnetic separator are a magnetic field strength, linear velocity and treatment temperature, and optimal conditions can be decided in compliance with the kind, size and concentration of iron particles to be magnetically attracted.

The magnetic field strength is the strength of the magnetic field in the space in which the filler is placed, and is usually within the range of 500 to 25,000 gauss, preferably 1,000 to 20,000 gauss.

The treatment temperature is the temperature of the oil at the time when it is introduced into the high gradient magnetic separator, and is usually within the range of room temperature to  $400^\circ\text{C}$ ., preferably room temperature to  $250^\circ\text{C}$ .

Further, the above mentioned linear velocity is the linear velocity of the oil passing through the magnetic field space, and is usually within the range of 0.1 to 50 cm/second, preferably 0.2 to 20 cm/second.

The lower the magnetic properties of the particles to be separated are, and the smaller the particle size is, the lower the linear velocity must be.



The particle concentration means a concentration of iron compounds contained and suspended in the oil and is usually within the range of about 0.001 to 10 g/l.

On the other hand, a drum type magnetic separator, which has heretofore been used for the separation of relatively large ferromagnetic particles in the field of the magnetic mineral dressing of an iron ore, has a magnetic field strength of 500 gauss and a magnetic field gradient of about 500 gauss/cm, which are much smaller than those of the high gradient magnetic separation of the present invention. Such a drum type magnetic separator cannot be employed to separate the iron content having a diameter of about 0.1 to 20 microns in the petroleum series mineral oil fraction, though being able to achieve the separation of iron particles as foreign substances each having a large diameter with which a catalyst is contaminated due to the corrosion or the erosion of a plant.

In the present invention, the petroleum series mineral oil fraction from which the iron content has been separated and removed can be subjected to a fixed-bed type hydrogenation treatment.

The fixed-bed type hydrogenation treatment is a method for converting the material oil into a useful oil by allowing the material oil to react with hydrogen under a high pressure at a high temperature in the presence of a catalyst so as to carry out decomposition, desulfurization and demetallation reaction. In short, the fixed-bed type hydrogenation treatment means the combination of a direct desulfurization, hydrogenolysis and the like.

As the catalyst for the hydrogenation treatment, there can be used a catalyst in which a hydrogenated metal component comprising a metal or a metallic compound in the group VI and/or the group VII such as cobalt-molybdenum, nickel-molybdenum, nickel-tungsten, cobalt-molybdenum-nickel or platinum is supported on a porous carrier such as an activated alumina, silica-alumina or silica-magnesia catalyst.

With regard to the conditions for the hydrogenation treatment process, the reaction temperature is from about 300.degree. to 480.degree. C., reaction pressure is from about 50 to 200 kg/cm.<sup>2</sup> (gauge), preferably from about 75 to 150 kg/cm.<sup>2</sup> (gauge), liquid space velocity is about 0.1 to 10 HR.<sup>-1</sup>, preferably from about 0.2 to 4 HR.<sup>-1</sup>, and the ratio of hydrogen/oil is about from 100 to 2,000 NI/l.

In the present invention, a gas containing hydrogen sulfide or a gas containing hydrogen sulfide and ammonia may be previously brought into contact with the petroleum series mineral oil fraction containing the iron content in order to convert the iron content contained therein into insoluble iron compounds, and the latter can be then separated and removed from the petroleum series mineral oil fraction by the use of the high gradient magnetic separator.

As the hydrogen sulfide gas and the ammonia gas used in the present invention, pure gases may be employed, but mixtures diluted with an inert gas such as hydrogen, nitrogen or methane may also be usable.

As the gas which will be brought into contact with the petroleum series mineral oil fraction in the present invention, an exhaust gas (an off-gas) usually obtained in a petroleum refining industry can be employed effectively.

That is, a catalytic hydrogenation refining process which is the most usual refining process for various petroleum hydrocarbon fractions serves to perform the hydrogenation of the mineral oil fraction, but in this case, sulfur and nitrogen of sulfur compounds and nitrogen compounds contained in the petroleum hydrocarbon fraction react with hydrogen under a high pressure at a high temperature in the presence of a catalyst. Then, they are discharged in the form of a hydrogen sulfide gas and an ammonia gas together with unreacted hydrogen and lower hydrocarbons from the hydrogenation refining reaction plant.



This gaseous mixture discharged from the hydrogenation refining reaction plant may be directly used as the mixed gas of the hydrogen sulfide gas and the ammonia gas effectively in the present invention. In addition, as this mixed gas, there can also be used a gas discharged at the time when the above reaction mixture from the reactor is subjected to a gas-liquid separation by the use of a high pressure separator and/or a low pressure separator. Further, a gas discharged in the case that the refined oil is stripped to expel the remaining gas can also be employed as the above mentioned mixed gas.

When concentrations of hydrogen sulfide and ammonia are within the range described above, the mixed gas can be, needless to say, used preferably, but the hydrogen sulfide gas and/or the ammonia gas can be additionally added to the above mentioned exhaust gas and then used.

The contact of the gas containing hydrogen sulfide or the gas containing hydrogen sulfide and ammonia with the petroleum series mineral oil fraction can be made by a gas-liquid mixing contact device such as a packed tower, a bubble-cap column or an orifice mixer, and with regard to a time necessary for the contact, a period of 1 to 120 minutes suffices.

A contact temperature is usually within the range of 10.degree. to 300.degree. C., preferably ordinary temperature to 200.degree. C., and when it is in excess of this upper limit, the removal percentage will be decreased rather than increased.

An amount of the gas used for the contact in the present invention is such that hydrogen sulfide per gram atom of iron contained in the mineral oil to be treated is usually within the range of 1 to 1,000 mols, preferably 5 to 600 mols.

When the ammonia gas is mixed with hydrogen sulfide, an amount of the ammonia gas is usually 1/2 mol or less, preferably 1/5 to 1/1,000 mol per mol of the hydrogen sulfide gas. If the device having a high contact percentage is used, the amount of the used gas can be reduced correspondingly.

The mineral oil fraction containing the iron content is brought into contact with the gas containing hydrogen sulfide and ammonia at a temperature between 10.degree. C. and 300.degree. C. in order to convert the iron content into insoluble iron compounds and to thereby deposit and suspend them in the oil. These insoluble iron compounds contain a large amount of iron sulfides but will not be decomposed by acidic materials in the oil.

The diameter of each particle of the insoluble iron compounds is mainly 10 .mu.m or less in a usual case, but at times, it is much smaller than 1 .mu.m. Usually, the insoluble iron compounds are present in the suspending state in the oil.

Afterward, the insoluble iron compounds which are deposited and suspended in the oil are removed by means of the high gradient magnetic separator.

In the present invention, after the gas containing hydrogen sulfide or the gas containing hydrogen sulfide and ammonia has been contacted with the petroleum series mineral oil fraction, the treatment may be then carried out by the high gradient magnetic separator, followed by the fixed-bed type hydrogenation treatment.

Preferred embodiments of the present invention will be described in reference to accompanying drawings.

In FIG. 1, reference numeral 1 is a high gradient magnetic separator, numerals 2 to 6 are on-off valves, 7

<http://patft.uspto.gov/netacgi/nph-Parser?Sect1=PTO1&Sect2=HITOFF&d=PALL&p=1&u=/n...> 3/4/02

to 11 are lines. Here, a petroleum series mineral oil fraction is introduced into the high gradient magnetic separator 1 through the line 7. At this time, the valves 4, 5 and 6 are closed and the valves 2 and 3 are opened. A portion of an iron content is magnetically attracted on a filler disposed in a magnetic field space in the high gradient magnetic separator 1.

When the operation is continued for a long period of time, the amount of the attracted iron content increases, so that the removal percentage of the iron content is lowered on occasion. In this case, the valves 2, 3 are closed, and the valve 4 is opened to by-pass the petroleum series mineral oil fraction. Afterward, the valves 5, 6 are opened, so that a washing oil is allowed to flow through the line 9 at an accelerated linear velocity, preferably at a speed ten times as high as at the treatment in a direction opposite to that at the time of the treatment, and immediately after this, the magnetic field is switched off. By this operation, the fine particles magnetically attracted by the filler are washed out and then discharged through the line 10. After a short period of time, the previous flowing state is re-established so as to restart the operation of the treatment.

In FIG. 2, reference numeral 1 is a high gradient magnetic separator, numerals 2 to 6 are on-off valves, 7 to 11 are lines. Here, a petroleum series mineral oil fraction is introduced into the high gradient magnetic separator 1 through the line 7. At this time, the valves 4, 5 and 6 are closed and the valves 2 and 3 are opened. A portion of the iron content is magnetically attracted on a filler disposed in a magnetic field space in the high gradient magnetic separator 1, and the petroleum series mineral oil fraction in which the iron content has been diminished is delivered to a hydrogenation treatment device 12 through the line 11.

When the operation is continued for a long period of time, the amount of the magnetically attracted iron content increases on the filler in the separator 1, so that the removal percentage of the iron content is lowered on occasion. In this case, the valves 2, 3 are closed, and the valve 4 is opened to cause the petroleum series mineral oil fraction to bypass. Afterward, the valves 5, 6 are opened, so that a washing oil is allowed to flow through the line 9 at an accelerated linear velocity, preferably at a speed ten times as high as at the treatment in a direction opposite to that at the time of the treatment, and immediately after this, the magnetic field is switched off. By this operation, the fine particles magnetically attracted by the filler are washed out and then discharged through the line 10. After a short period of time, the previous flowing state is re-established so as to restart the operation of the treatment.

In FIG. 3, reference numeral 13 is a gas-oil contact device, numeral 1 is a high gradient magnetic separator, numerals 2 to 6 are on-off valves, 7 to 11 are lines. Here, a material oil introduced into the contact device 13 through a line 7 is brought into contact with a gas coming through a line 14 therein, so that insoluble iron compounds are deposited. Numeral 8 is a by-pass line, which is usually closed. The oil which has been brought into contact with the gas is delivered to the high gradient magnetic separator 1, and is then subjected to treatment. The deposited iron content and the other iron content are magnetically attracted on a filler disposed in a magnetic field space in the high gradient magnetic separator 1.

When the operation is continued for a long period of time, the amount of the magnetically attracted iron content increases on the filler in the separator 1, so that the removal percentage of the iron content is lowered on occasion. In this case, the valves 2, 3 are closed, and the valve 4 is opened to by-pass the petroleum series mineral oil fraction. Afterward, the valves 5, 6 are opened, so that a washing oil is allowed to flow through the line 9 at a relatively high linear velocity, preferably at a speed ten times as high as at the treatment in a direction opposite to that at the time of the treatment, and immediately after this, the magnetic field is switched off. The fine particles magnetically attracted by the filler are thereby washed out and then discharged together with the washing oil through the line 10. Afterward, the previous flowing state is re-established so as to restart the operation of the treatment.

The present invention will be described in detail in reference to examples.

### EXAMPLE 1

By the use of an electromagnetic type high gradient magnetic separator "SALA-HGMS" (registered trademark), a petroleum series vacuum residual oil was treated under the following conditions:

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Magnetic field strength:	20 kilogauss
Linear velocity:	3.0 cm/sec
Temperature:	150.degree. C.
Filler:	Steel wool

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With regard to the thus treated oil and the material oil, iron contents were measured. The results are set forth in Table 1.

TABLE 1

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	Material oil	Treated oil
Iron content (wt ppm)	30.0	8.3
Removal percentage (%)	--	72.3

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The respective oils shown in Table 1 were subjected to a hydrogenation treatment by the use of a catalyst in which Mo, Co and Ni were supported on an alumina carrier, an amount of each component of Mo, Co and Ni being 5 wt. % based on the carrier. Conditions were as follows:

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Reaction temperature:	400.degree. C.
LHSV:	0.3 hr.sup.-1
Partial pressure of hydrogen:	120 kg/cm.sup.2
Reaction time:	4,000 hours

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After the reaction, the catalyst and deposited substances were taken out from the upper portion, the middle portion and the lower portion of the reaction tower. Calcinating was then carried out, and the total Fe amount of the catalyst and the deposited substances in each portion was measured. The results are set forth in Table 2.

TABLE 2

Charge stock	Material oil	Treated oil
Upper portion (wt %)	11.5	2.1
Middle portion (wt %)	1.8	1.1
Lower portion (wt %)	0.7	0.5

The results set forth in Table 2 indicate that when the oil treated by the high gradient magnetic separator is used as the material, the amount of the iron on the catalytic bed in the upper portion of the reaction tower is decreased remarkably.

## EXAMPLE 2

Commercially available iron naphthenate was dissolved in 70 pale of a fraction to prepare a material oil in which the iron content was 100 ppm.

As a contact treatment device, a packed tower was employed which had an inner diameter of 75 mm and a height of 2,000 mm, and as a filler, 5.0 liters of a percelain Raschig ring (10 mm in diameter) were employed.

The above mentioned material oil (feed rate 5 l/hr) at ordinary temperature was allowed to stream down from the top of the packed tower so as to accomplish a counter flow contact with an off-gas (feed rate 100 l-STP/hr) at ordinary temperature coming up from the bottom of the tower through a hydrogenation refining device under conditions of ordinary temperature and ordinary pressure, the aforesaid off-gas having the following composition. The material oil thus treated was afterward taken out from the tower through the bottom thereof.

Hydrogen (vol %):	73.8
Hydrogen sulfide (vol %):	2.1
Ammonia (vol %):	0.01
Light saturated hydrocarbon	24.09
(vol %) (C.sub.1 to C.sub.4):	

The thus treated oil was further treated by the use of SALA-HGMS (registered trademark) under the following conditions:

Magnetic field strength:	10 kilogauss
Linear velocity:	10 cm/sec
Temperature:	Ordinary temperature
Filler in magnetic field space:	

## Steel wool

## COMPARATIVE EXAMPLE 1

The treated oil which was prepared in Example 2 was filtered through a No. 5 filter paper.

## COMPARATIVE EXAMPLE 2

The treated oil which was prepared in Example 2 was centrifuged to separate solids in the oil therefrom.

The oils prepared in Example 2 and Comparative Examples 1 and 2 were then analyzed, and removal percentages were calculated from the concentrations of iron. The results are set forth in Table 3.

TABLE 3

	Example	Comp. Ex. 1	Comp. Ex. 2
Iron content (ppm)	25	28	32
Removal percentage	75.0	72	68
of iron content (%)			
Total acid value	0.22	0.23	0.22
(mg-KOH/g)			

## EXAMPLE 3

A petroleum series vacuum residual oil was treated by the permanent magnet type high gradient magnetic separator under the following conditions:

Magnetic field strength:	1 kilogauss
Linear velocity:	0.5 cm/sec
Temperature:	250.degree. C.
Filler:	Steel beads

With regard to the thus treated oil and the material oil, iron contents were measured. The results are set forth in Table 4.

TABLE 4

Material oil	Treated oil
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Iron content (wt ppm)		
	42.0	17.0
Removal percentage (%)		
--		59.5

The results in Table 4 indicate that the permanent magnet type high gradient magnetic separator can provide about the same removal effect of the iron content as in the case of the electromagnet type high gradient magnetic separator.

As described in Example 1, if the material oil is reacted without any treatment, much iron will be deposited in the upper portion of the catalyst bed in the reactor, so that clogging and increase in pressure will be caused. In consequence, stopping of the plant will be inevitable at times, and a large disadvantage will arise. According to the present invention, these troubles can be prevented, and the operation of the plant can be continued till the activity of the catalyst has passed away or as planned.

As seen in Table 3, the method of the present invention can provide the improved removal percentage of iron as compared with the comparative examples.

Further, in the method of the present invention, extremely rapid separation and removal are possible, and the treatment speed is several thousand times or more as high as that of the comparative examples.

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# US PATENT & TRADEMARK OFFICE

## PATENT FULL TEXT AND IMAGE DATABASE



( 1 of 1 )

United States Patent  
Jody , et al.

5,653,867  
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Method for the separation of high impact polystyrene (HIPS) and acrylonitrile butadiene styrene (ABS) plastics

### Abstract

An improved method is provided for separating acrylonitrile butadiene styrene (ABS) and high impact polystyrene (HIPS) plastics from each other. The ABS and HIPS plastics are shredded to provide a selected particle size. The shredded particles of the ABS and HIPS plastics are applied to a solution having a solution density in a predefined range between 1.055 gm/cm.sup.3 and 1.07 gm/cm.sup.3, a predefined surface tension in a range between 22 dynes/cm to 40 dynes/cm and a pH in the range of 1.77 and 2.05. In accordance with a feature of the invention, the novel method is provided for separating ABS and HIPS, two solid thermoplastics which have similar densities by selectively modifying the effective density of the HIPS using a binary solution with the appropriate properties, such as pH, density and surface tension, such as a solution of acetic acid and water or a quaternary solution having the appropriate density, surface tension, and pH.

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**Intern'l Class:** B03B 001/04; B03B 005/28; B03D 001/02

**Field of Search:** 209/9,164,166,173 241/24.18,24.28 521/40.5,41,43.5

### References Cited [Referenced By]

#### U.S. Patent Documents

1195264

Aug., 1916

Pennigton.

<u>3985650</u>	Oct., 1976	Saitoh.
<u>4119533</u>	Oct., 1978	Saitoh.
<u>4132633</u>	Jan., 1979	Saitoh.
<u>4167477</u>	Sep., 1979	Valdez.
<u>5377844</u>	Jan., 1995	Hwang.
<u>5399433</u>	Mar., 1995	Kobler.
<u>5566832</u>	Oct., 1996	Stuckrad.

### Other References

Buchan, R. and Yarar, B., "Recovering Plastics For Recycling by Mineral Processing Techniques", Feb. 1995, JOM, pp. 52-55.

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### Government Interests

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### CONTRACTUAL ORIGIN OF THE INVENTION

The United States Government has rights in this invention pursuant to Contract No. W-31-109-ENG-38 between the United States Government and Argonne National Laboratory.

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### Claims

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What is claimed is:

1. A method for separating acrylonitrile butadiene styrene (ABS) and high impact polystyrene (HIPS) plastics from each other comprising the steps of:

shredding the ABS and HIPS plastics to provide a selected particle size; and

applying the shredded particles of the ABS and HIPS plastics to a solution having a solution density in a predefined range between 1.055 gm/cm.<sup>3</sup> and 1.07 gm/cm.<sup>3</sup>, a predefined surface tension in a range between 22 dynes/cm to 40 dynes/cm and a pH in the range of 1.77 and 2.05 wherein the plastics separate from each other by the high impact polystyrene (HIPS) forming a floating fraction in the solution and the acrylonitrile butadiene styrene (ABS) forming a sink fraction.

2. A method for as recited in claim 1 wherein said step of applying the shredded particles of the ABS and HIPS plastics to said solution includes the step of providing a solution of acetic acid and water.

3. A method for as recited in claim 1 wherein said step of applying the shredded particles of the ABS and HIPS plastics to said solution includes the step of providing a solution of approximately equal parts of acetic acid and water by volume.



4. A method for as recited in claim 1 wherein said step of shredding the ABS and HIPS plastics to provide said selected particle size includes the step of shredding the ABS and HIPS plastics to provide said particle size of about 6.5 mm.

5. A method for as recited in claim 1 wherein said step of applying the shredded particles of the ABS and HIPS plastics to said solution includes the step of providing a quaternary solution of hydrochloric acid, sodium chloride, water and a surfactant.

6. A method for as recited in claim 1 wherein said step of applying the shredded particles of the ABS and HIPS plastics to said solution includes the step of providing a quaternary solution of hydrochloric acid, calcium chloride, water and a surfactant.

7. A method for as recited in claim 1 wherein said step of applying the shredded particles of the ABS and HIPS plastics to said solution includes the step of providing a quaternary solution of hydrochloric acid, water soluble salts, water and a surfactant.

8. A method for as recited in claim 1 further includes the step of washing the ground particles of ABS and HIPS plastics prior to applying the shredded particles to the solution.

9. A method for as recited in claim 1 further includes the step of separating the shredded particles of ABS and HIPS plastics from lighter materials with a flotation stage having a specific gravity of about 1.0 prior to applying the shredded particles to said solution.

10. A method for as recited in claim 1 further includes the step of separating the shredded particles of ABS and HIPS plastics from heavier materials with a flotation stage having a specific gravity of about 1.10 to 1.125.

11. A method for separating acrylonitrile butadiene styrene (ABS) and high impact polystyrene (HIPS) plastics from each other comprising the steps of:

shredding the ABS and HIPS plastics to provide a selected particle size; and

applying the shredded particles of the ABS and HIPS plastics to a binary solution of acetic acid and water having a solution density in a predefined range between 1.055 gm/cm.<sup>3</sup> and 1.07 gm/cm.<sup>3</sup>, a predefined surface tension in a range between 22 dynes/cm to 40 dynes/cm and a pH in the range of 1.77 and 2.05 wherein the plastics separate from each other by the high impact polystyrene (HIPS) forming a floating fraction in the solution and the acrylonitrile butadiene styrene (ABS) forming a sink fraction.

12. A method for separating acrylonitrile butadiene styrene (ABS) and high impact polystyrene (HIPS) plastics from each other comprising the steps of:

shredding the ABS and HIPS plastics to provide a selected particle size; and

applying the shredded particles of the ABS and HIPS plastics to a quaternary solution having a solution density in a predefined range between 1.055 gm/cm.<sup>3</sup> and 1.07 gm/cm.<sup>3</sup>, a predefined surface tension in a range between 22 dynes/cm to 40 dynes/cm and a pH in the range of 1.77 and 2.05 wherein the plastics separate from each other by the high impact polystyrene forming a floating fraction in the solution and the acrylonitrile butadiene styrene (ABS) forming a sink fraction.

13. A method for as recited in claim 12 wherein said step of applying the shredded particles of the ABS and HIPS plastics to said quaternary solution includes the step of providing a quaternary solution of hydrochloric acid, calcium chloride, water and a surfactant.

14. A method for as recited in claim 12 wherein said step of applying the shredded particles of the ABS and HIPS plastics to said quaternary solution includes the step of providing a quaternary solution of hydrochloric acid, sodium chloride, water and a surfactant.

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### *Description*

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## BACKGROUND OF THE INVENTION

### 1. Field of the Invention

The present invention relates to an improved method for the separation of different types of plastics, and more particularly to an improved process for the separation of acrylonitrile butadiene styrene (ABS) and high impact polystyrene (HIPS) plastics from each other.

### 2. Description of the Prior Art

Recycling of different types of plastics has increased in recent years. Processes for separating different plastic types have become increasingly important. For example, "Recovering Plastics for Recycling by Mineral Processing Techniques," by R. Buchan and B. Yarar, JOM, February, 1995, pps. 52-55, discloses a process for separating plastics by use of a mineral processing technology.

U.S. Pat. No. 5,399,433, issued Mar. 21, 1995 to Kobler, discloses a method for separating a polyethylene terephthalate (PET)/polyvinyl chloride (PVC) chip admixture. The PET/PVC chip admixture is contacted with a surface conditioning agent to produce relatively hydrophobic polyvinyl chloride chips which can be floated in an aerated aqueous medium. The polyethylene terephthalate chips are recovered from the bottom of the aqueous medium. The flotation is conducted in pure water without frothing or densifying agents.

Separation of solids using differences in their densities is a simple, economical and effective technique. A liquid whose density is between the densities of two solids can be used as the working medium. The solid with the lesser density floats and the solid with the higher density sinks resulting in the separation of the mixture. However, materials that have similar densities, such as acrylonitrile butadiene styrene, ABS, and high impact polystyrene, HIPS, can not be separated in high purities by this simple and inexpensive technique.

Different grades of both of the ABS and HIPS plastics have specific gravities in the range of 1.055 to 1.125. As a result such mixtures can not be effectively separated by density gradient procedures. Attempted separation of ABS and HIPS plastics by the inventors in their laboratory using conventional density gradient procedures has produced ABS product that is about 95% pure. However, 5% HIPS impurity in the ABS resulted in severe degradation of its properties, specifically its tensile and impact strengths because the two plastics are not compatible.

The recycling of white goods such as refrigerators in the United States and Europe involves the shredding of the refrigerators after the removal of the bulk refrigerants. The metallic content of the shredded material is then separated and recycled, and the non-metallic residue is considered waste, and

is presently land filled. The two dominant plastics in refrigerators are acrylonitrile butadiene styrene (ABS) and high impact polystyrene HIPS. Other plastics may also be present, such as polypropylene, polyethylene, nylons and polyvinyl chloride. Many of these plastics can be separated from each other and from HIPS and ABS utilizing differences in density. Because ABS and HIPS have similar densities, ABS and HIPS are not separable by this method. ABS and HIPS are not compatible and a small amount of contamination of one in the other severely restricts its commercial value. One method that we successfully tested for separating HIPS from ABS takes advantage of the selective stickiness of the materials generated by solvents. While this method may be effective in separating the two plastics, the use of quantities of organic solvents has environmental drawbacks. Another technique that may be used for separating HIPS and ABS involves contacting the mixture with a surface that is heated to a temperature high enough for HIPS to stick to the hot surface but not hot enough for ABS to become sticky. Continuous cleaning of the hot surface is necessary to prevent sticking of the ABS to spots on the hot surface that have residual sticky HIPS.

It is an object of the present invention to provide an improved method process for the separation of acrylonitrile butadiene styrene (ABS) and high impact polystyrene (HIPS) plastics from each other.

It is another object of the present invention to provide such an improved method for separating ABS and HIPS plastics without requiring the use of organic solvents, and at ambient conditions to minimize energy consumption.

It is another object of the present invention to provide such an improved method that provides reliable and effective operation.

It is another object of the present invention to provide such an improved method that overcomes many of the disadvantages of prior art arrangements.

## SUMMARY OF THE INVENTION

In accordance with these and other objects of the invention, an improved method is provided for separating acrylonitrile butadiene styrene (ABS) and high impact polystyrene (HIPS) plastics from waste streams and from each other. The ABS and HIPS plastics are shredded to provide a selected particle size. The shredded particles of the ABS and HIPS plastics are applied to a solution having a solution density in a predefined range between 1.055 gm/cm.<sup>3</sup> and 1.07 gm/cm.<sup>3</sup>, a predefined surface tension in a range between 22 dynes/cm to 40 dynes/cm and a pH in the range of 1.77 and 2.05.

In accordance with a feature of the invention, the novel method is provided for separating ABS and HIPS, two solid thermoplastics which have similar densities by selectively modifying the effective density of the HIPS using a solution having the appropriate density, surface tension, and pH, such as acetic acid and water or hydrochloric acid, salt, surfactant and water. The acetic acid used in substantial mass ratios (50/50 volume basis) can achieve the desired surface tension, pH and density. Hydrochloric acid is used in small quantities to achieve the desired pH. A water soluble salt such as sodium chloride or calcium chloride can be used to raise the density and a surfactant can be added in minute quantities to achieve the desired surface tension. Other organic and inorganic acids can be substituted for the acetic and the hydrochloric acids as long as the surface tension, density and pH are maintained in the desired ranges. We conducted experiments with acetic acid, hydrochloric acid, sodium chloride, calcium chloride, and surfactants. The results were reproducible when the pH, density and surface tension were in the prescribed ranges. Each produced >99% pure ABS. Greater than 99% pure HIPS was also produced in one or two steps. The pure ABS was produced in a single step. The yields of ABS and of HIPS were greater than 90%. This was achieved at ambient temperature and pressure.

## BRIEF DESCRIPTION OF THE DRAWINGS

The present invention together with the above and other objects and advantages may best be understood from the following detailed description of the preferred embodiments of the invention illustrated in the drawings, wherein:

FIG. 1 is a process flow diagram illustrating apparatus for performing sequential steps of the process for the separation of acrylonitrile butadiene styrene (ABS) and high impact polystyrene (HIPS) plastics from a waste stream produced from obsolete refrigerators and from each other in accordance with the present invention; and

FIG. 2 is a chart illustrating density of acetic acid water solutions with different mass ratios along the vertical axis relative to temperature along the horizontal axis;

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to FIG. 1, there is shown a schematic and block diagram representation of a material processing system used for the effective separation of acrylonitrile butadiene styrene (ABS) and high impact polystyrene (HIPS) plastics from a waste stream and from each other in accordance with the invention generally designated by the reference numeral 10. A waste stream containing at least the ABS and HIPS solid thermoplastics is applied to a shredding stage 12 and is ground to a selected size, for example, 0.25 inch or about 6.5 mm. The shredding step at stage 12 facilitates the liberation of rigid foam from refrigerator plastic-liner materials. After shredding, the material is washed with water and surfactants at a washing stage 14 to remove dirt and any residual oils. To enhance the cleaning step, the waste stream is agitated at the washing stage 14. The waste stream being processed is applied to a rinsing stage 14A, after the washing stage 14. The waste water resulting from the washing stage 14 is applied to a filter and water treatment stage 16 where the waste water is first filtered to trap its solids contents and then treated and fed back to the washing stage 14 to be reused. The filter and water treatment step at stage 16 is used to minimize the generation of waste water. A first flotation stage 18 where the specific gravity is maintained at approximately 1.0 separates light materials, such as foam, polypropylene (PP) and polyethylene (PE) from the heavier materials. The washing stage 14 can be used as the first floatation stage, unless the feed material is excessively dirty to the point where the density in the wash tank changes rapidly. Paddle wheels or wipers can be used at the first flotation stage 18 to skim any floaters out of the tank and drop them on a screen to drain. Water that drains from the light materials can be pumped back into the stage 18. Foam can be separated from the PP and PE in a flotation stage 20 having a specific gravity between 0.7 and 0.85 or using other means such as hydrocyclones.

The washed heavy materials are then separated into two fractions by a flotation stage 22 having a specific gravity maintained at about 1.10-1.15. Operating at a specific gravity closer to 1.10 will decrease the ABS and HIPS yields but will guard against contamination of the ABS and HIPS products with other plastics such as nylons, that are commonly used in home appliances. The high value plastics, ABS and HIPS are the first fraction. The second fraction contains the heavier constituents of the waste stream, such as PVC, nylons, and the residual metals. Both ABS and HIPS have specific gravities in the range of 1,055 and 1,125 and cannot be separated from each other in high purity by using conventional gravity-separation techniques. In a preferred arrangement, an acid and water solution at ambient temperature and pressure having a pH of about 1.77, a surface tension of about 22-40 dynes/cm and a density of about 1,067 gm/cm<sup>3</sup>, such as an acetic acid and water solution 24 having air bubbles passed upwardly through the solution is used for separating the mixture of HIPS and ABS. The air bubbles adhere to the HIPS, carrying the HIPS to the surface of the solution while the ABS remains at the bottom of the container. Introduction of air bubbles is not always required. As a matter of fact, when acetic acid or hydrochloric acid is used we did not need to introduce air to get good separation. Even

when needed it should be administered at low enough velocities and bubble sizes to avoid disturbing the settling ABS chips. Operating at higher surface tension values ( $>40$  dynes/cm and up to  $\sim 45$  dynes/cm) is also possible, but the stability of the settling ABS chips is reduced as the surface tension is increased. Operation at surface tension values of 22-30 is preferred. Surface tension values less than 22 also resulted in reducing the purity of the products. A third flotation stage 26 having a specific gravity of about 1.35 separates the PVC and nylons from the mixed metals.

In brief summary, our experimental data verifies that ABS and HIPS streams, each having a purity greater than 99%, can be separated from a HIPS/ABS mixture with over 90% yield of each at ambient temperatures ( $18^{\circ}\text{C}$ .- $28^{\circ}\text{C}$ .) and in a single step, or in two steps when several grades of these species are present, using aqueous solutions having densities in the range of 1.055 to 1.07 grams/milliliter, and having surface tension values in the range of 22 to 40 dynes/centimeter, and a pH in the range of 1.77-2.05. The appropriate combination of these parameters have to be used to get products with  $>99\%$  purity and  $>90\%$  yield, demonstrated using solutions containing:

Acetic acid or hydrochloric acid

Sodium or calcium chloride

Surfactants, and

Water

We realize that other aqueous solutions containing organic or inorganic acids and other salts and surfactants that can generate the right operating conditions can also be used to achieve the same goals.

## EXPERIMENTAL OBSERVATIONS

While conducting small scale experiments on HIPS and ABS exposed to acetic acid and acetic acid/water solutions, it was observed that when a mixture of these solids was introduced into glacial acetic acid (liquid at room temperature), a significant portion of the HIPS floated while the ABS sank. The ABS, the HIPS and the glacial acetic acid all have a density of about  $1.055\text{ g/cm}^3$ . The same behavior was later observed when a mixture of these solids was dropped in a 50/50 (volume basis) acetic acid/water solution. The tests were repeated using recycled HIPS and ABS obtained from scrapped refrigerators that had densities of about 1.055 to  $1.125\text{ g/cm}^3$ . The same results as with the virgin materials were observed.

Examination of the HIPS and ABS solids during these tests, while in the solution under a magnifying glass showed that the surface of the HIPS particles was covered with one or more layers of tiny gas bubbles. The surface of the ABS particles contained very few scattered bubbles. This phenomenon reduced the effective density of the HIPS particles below that of the solution and thus the HIPS floated, while the density of the ABS particles was maintained above that of the solution. The addition of the acetic acid to the water reduced the surface tension, having the effect of a surfactant, while increasing the density and reducing pH. When a mixture of recycled HIPS and ABS was dropped into a 20/80 (volume basis) solution of acetic acid/water, both solids sank. This is an indication that the density of the solution has dropped below the apparent density of the gas-bubbles-coated HIPS particles. The addition of a surfactant to the 50/50 solution, in which the HIPS has been separated from the ABS, resulted in HIPS sinking along with the ABS. This is an indication that the layers of gas bubbles on the HIPS have been lost as the surface tension dropped below a certain level.

We concluded from the test results in that a liquid having the appropriate surface tension, pH, viscosity

and density can be used to separate HIPS and ABS which have similar densities but have different surface interactions with the liquid solution. The principle described here can be used to separate a variety of solid mixtures using a liquid having the appropriate surface tension, pH, viscosity and density, where the solids have different surface interactions with the liquid solution. This principle can also be used as a polishing step for many density gradient based separation methods.

The acetic acid/water solution we used was somewhat unique because the appropriate pH, density, surface tension and viscosity were achieved using a binary solution. We also achieved similar results using a quaternary solution of hydrochloric acid, sodium chloride, water and a surfactant. For example, a description of one test with a quaternary solution follows. About 2 liters of tap water were placed in a three liter beaker. Sodium chloride was added to the water until the solution density was increased to about 1.067 gm/cm.<sup>3</sup>. A small amount of a surfactant was added to the solution to reduce its surface tension to between 22 and 32 dynes/cm in different experiments. Concentrated hydrochloric acid (37% solution) was then added to bring the pH of the solution down to about 1.77 while the solution was being mixed by agitation. A mixture of about 250 grams of post consumer product HIPS and ABS in the form of approximately 0.25 inch chips, that was produced from obsolete refrigerators and from which metals, foam, nylons and PVC had been separated, was then added to the solution. The solution and its contents were then stirred for about 30 seconds and allowed to settle. In less than one minute a fraction of the added plastics floats and another fraction sinks. The two fractions were collected and analyzed piece by piece using an FTIR machine. The results showed over 99% pure ABS in the fraction that sunk.

We conducted experiments on mixtures of recycled HIPS and ABS using acetic acid/water solutions at acetic acid to water mixing volume ratios in the range of 0 (no acetic acid) to 1 (no water). We also varied the temperature to alter the density at a given solution composition. Analysis of the ABS fraction produced from these experiments showed that ABS fractions having greater than 99% purity (less than 1% HIPS) were produced in a single pass when the solution density was in the range of 1.055 and 1.067 gm/cm.<sup>3</sup>, and the pH was in the range of 1.77 and 2.05. Acetic acid solutions that had these properties had surface tension values in the range of 30 to 40 dynes/cm. The changes in viscosity were minimal. Hips fractions having greater than 99% purity (less than 1% ABS) were also produced using solutions having properties in the ranges specified above in one or two passes and using one or two solutions, depending upon the number of different grades of each plastic present. The yields on ABS and HIPS were greater than 90%. We like to point out here that the recycled ABS/HIPS stream contains many different grades of these plastics that were produced over a number of years and by more than one manufacturer.

We identified a range of operating conditions that produce ABS and HIPS products having greater than 99% purity. These products can be upgraded using commercially available modifiers to raise the properties of the recycled material close to those of their virgin counterparts. We demonstrated the appropriateness of these operating conditions by achieving similar results using a quaternary solution of hydrochloric acid, sodium chloride, water, and a surfactant.

While the present invention has been described with reference to the details of the embodiments of the invention shown in the drawing, these details are not intended to limit the scope of the invention as claimed in the appended claims.

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